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**A Case Study of Water Distribution Management
Options for the Reduction of Trihalomethane Formation
at the U.S. Naval Station on the island of Santo Stefano, Italy**

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CE 698
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Abstract of Major Findings

- Chlorine dioxide (ClO_2) treatment can provide a secondary disinfectant residual, but not a very persistent residual. ClO_2 treatment at the main water treatment plant (ESAF) has left a free chlorine residual (Cl_2) of 0.25-mg/l (from inefficiencies in the formation of ClO_2) present at the U.S. Navy tank influent and therefore re-disinfection is required to provide a disinfectant residual.

- The Santo Stefano water likely has a high bromide concentration. The concentration was estimated to be 0.3-mg/l by using equations from Amy, Chadik and Chowdhury (1987) and laboratory data for TTHMFP performed on the Santo Stefano U.S. Navy tank influent.

- The fitted TTHMFP curve predicted by the Amy, Chadik, and Chowdhury equation at a bromide concentration of 0.3-mg/l can be used to determine how varying pH, contact time, and chlorine dose might affect the TTHMFP of the Santo Stefano water.

- Reducing the pH from 7.8 to 6.5 failed to reduce the TTHM formation to below 30- $\mu\text{g/l}$ even after 1 day (Figure 2.5), as predicted by the Amy et al. equation.

- Reducing the pH from 7.8 to 7 and Cl_2 dose to 1 mg/l (a dose expected to last 3 days in the Santo Stefano distribution system) in the Amy et al. equation predicts a reduction of the TTHM formation at 1-day retention time below 30- $\mu\text{g/l}$. Reductions in detention times of this magnitude are unlikely due to limited water capacity during summer months.

- Free chlorine contact time of over 3hrs is likely allowable at a chlorine dose of 3-mg/l without exceeding 30- $\mu\text{g/l}$ TTHM's. Concurrent addition of ammonia and free chlorine would only provide a free chlorine contact time of up to 5 minutes. Therefore, a 3-mg/l dose of chloramines is a likely, cost effective solution.

- GAC filtration designed with a service time to allow a 10% - 20% breakthrough of TOC should allow for free chlorine doses of up to 3-mg/l at detention times of up to 6 days in the distribution system without exceeding 30- $\mu\text{g/l}$ TTHM's in the Santo Stefano distribution system. Whether GAC filtration could reach the model predicted TOC concentration of 0.2 to 0.4 mg/l is doubtful. GAC filtration may not have to be this thorough if model predictions of TTHM formation are high.

- An unknown quantity of chlorites (ClO_2^{-1}) is surely present at Santo Stefano from the chlorine dioxide treatment at ESAF and will likely have a negative impact on GAC service time.

1.0 Introduction

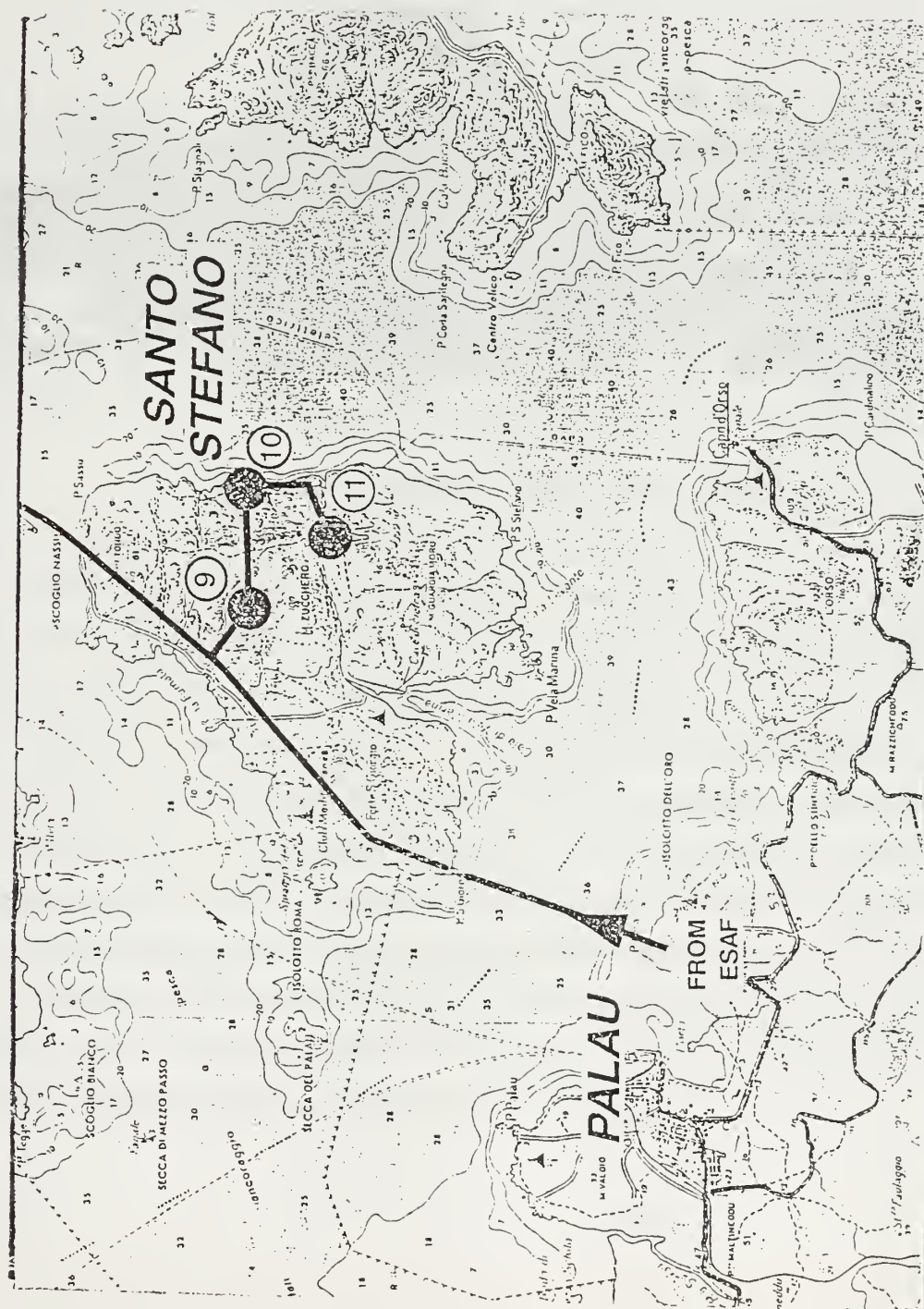
1.1 Background Information/ Problem Statement

The U.S. Naval Station - Santo Stefano is located on the island of Santo Stefano, Italy at the northern tip of the island of Sardinia (see Figure 1.1). Just north of the island of Santo Stefano is the island of La Maddalena, which also hosts U.S. Naval facilities. All three Italian islands are located just west of the Italian mainland.

Over the past several years there have been many incidences of non-compliance with local and U.S. water quality standards at all U.S. Naval facilities located on the aforementioned islands. The major issue of non-compliance is the high level of trihalomethanes (THM's) that are produced wherever there are chlorine booster stations located at the U.S. Naval facilities. For the purpose of this report, water distribution system management will be analyzed with respect to the Naval Station – Santo Stefano. Various solutions to the water quality problems will be discussed with regards to applicability and cost. This report examines the distribution system management, disinfection, and treatment.

1.2 Water Supply System

The Liscia Reservoir, fed by the Liscia River, is the source of water supply to the island of Santo Stefano. Water is supplied to the island of Santo Stefano from the Agnata-Liscia Water Treatment Plant, which is owned and operated by the Italian Regional Water Supply Authority or Ente Sardo Acquedotti Fognature (ESAF). The treated water from ESAF is supplied to the U.S. Naval Station- Santo Stefano via a 16-inch underwater transmission line as shown in Figure 1.2. From the 16-inch water main, a 6-inch line branches off via a tee connection and runs uphill to the 1000 metric ton (MT) – 263,300 gallon Santo Stefano Tank. The Santo Stefano tank is a buried reinforced-concrete structure. From this tank water flows by gravity through two pipelines; a 4-inch pipeline feeds the Club Valtur tank and a 6-



Facility Location

- 9 Santo Stefano Tank
- 10 U.S. Navy Tank
- 11 Italian NATO Support Tank

Figure 1.2 – Water Distribution to Santo Stefano

inch diameter pipe feeds the U.S. Navy tank and the Italian NATO support tank. A simplified elevation diagram of this is shown in Figure 1.3 below.

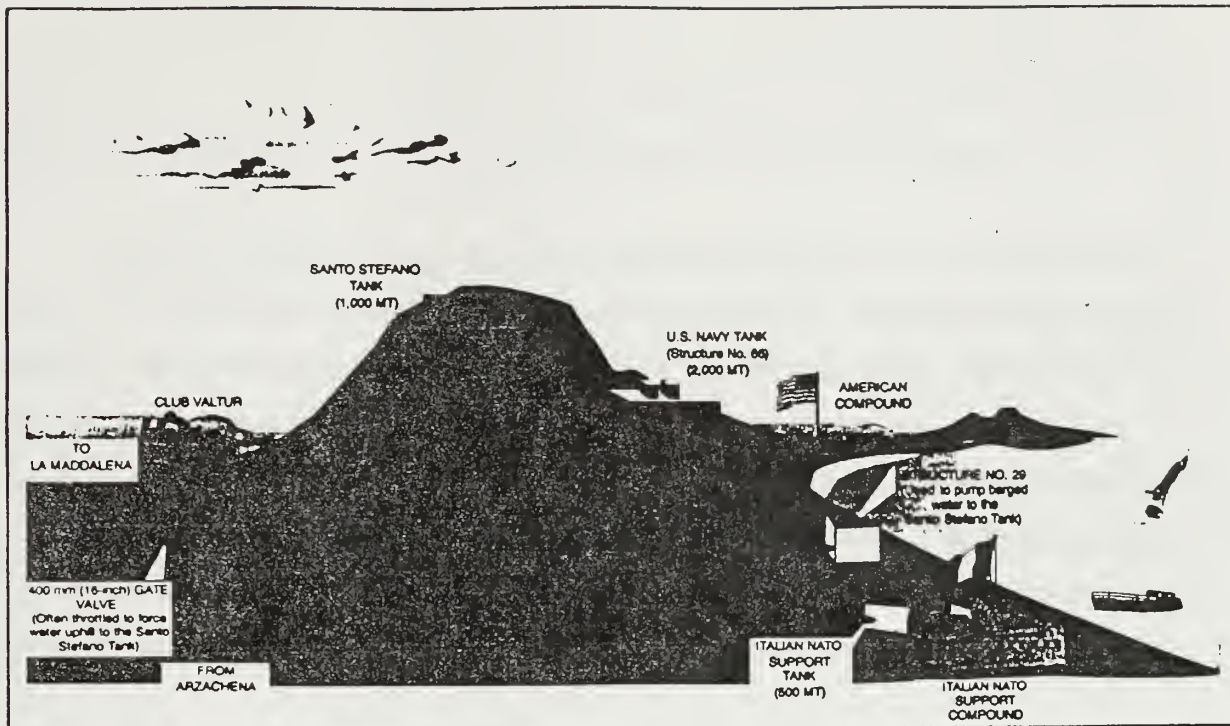


Figure 1.3 - Elevation Diagram –Santo Stefano

The U.S. Navy tank is located on a hillside at an elevation of approximately 60 meters above sea level. The U.S Navy tank is a 2000 MT – 526,600 gallon partially buried reinforced-concrete structure that is separated into two compartments. The compartments are further divided into two cells. A U.S. Navy Tank Schematic is shown in Figure 1.4. Barging of comparable quality water from other areas on Sardinia is sometimes accomplished in the summer tourist season. This limits how much the U.S. Navy storage can be reduced since the barges are 600 to 1000 MT. The need for barging water in recent years has almost completely diminished, and the water quality effects are minimal since water of comparable quality is brought in when required. The impact to this project, however, is that the U.S. Navy tank storage provided cannot be reduced significantly due to the critical need for the U.S. Navy water supply for homeported submarines, and ships.

Water treatment at ESAF consists of both pre-disinfection and post-disinfection with chlorine dioxide (ClO_2). The water is first sent through a microscreen, then alum coagulation is utilized to remove particulate organics. The water is then filtered through both sand and granular activated carbon (GAC). This treated water is sent to Santo Stefano at the rate of approximately 792.5 gpm or 1.15 mgd. Water treated at ESAF is also sent to La Maddalena via the 16" pipeline (Figures 1.2 and 1.3) that conveys water to Santo Stefano.

Supplemental chlorination is provided for additional disinfection prior to storage in the U.S. Navy tank. The free chlorine feed equipment consists of a chemical metering pump, 50-gallon sodium hypochlorite storage containers, and automated controls that regulate the chlorine feed based on influent flow to the U.S. Navy tank. Adjustments are made to maintain a 0.5 mg/L free chlorine residual in the distribution system. It is this free chlorine booster station that is the source of excessive THM's at Santo Stefano. This supplemental chlorination is required since the free chlorine residual (as a result of the inefficiencies in the production of ClO_2) is only 0.25 mg/l at the U.S. Navy tank influent.

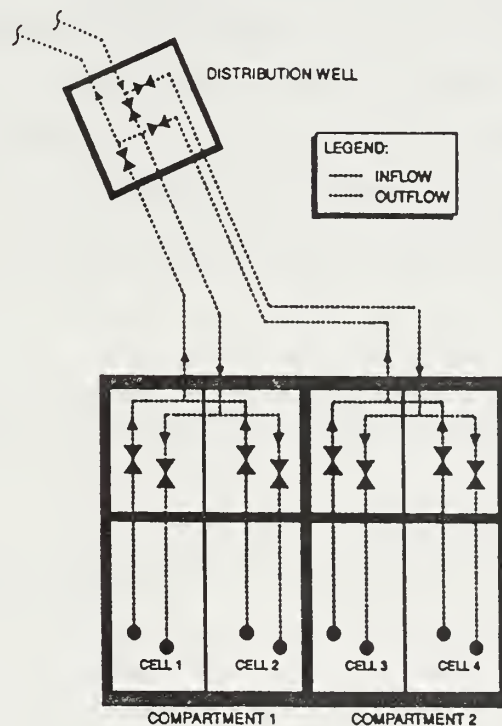


Figure 1.4 - U.S. Navy Tank Schematic

1.3 Santo Stefano Water Demand

A knowledge of the water system demand is required in addition to a knowledge of the water supply and storage if an analysis of the water distribution system management is to be performed. Water demand at Santo Stefano varies widely due to a varying number of ships in port. The U.S. Navy can have as many as 3 submarines and 1 tender ship in port at any given time, or there may be none in port.

U.S. Navy activities constitute roughly 85% of the total site water usage at Santo Stefano. Total site usage therefore is a rough approximation of the U.S. Navy usage. For instance, the peak total site usage experienced in 1994 and 1995 was 873 MT on August 9, 1995 as can be seen in Figure 1.6. Since likely greater than 85% of this flow was due to the U.S. Navy ships in port, this is a good indication of the maximum U.S. Navy water demand that can be expected. If the daily water demand is ranked in order of increasing value from the 1994 – 1995 water demand tables shown in figures 1.5 and 1.6 then a 90 percentile flow of approximately 470 MT/day (86 gpm) can be determined. This is a good indication of U.S. Navy water demand during a typical high flow condition. Similarly, a 25 percentile flow of 133 MT/day (24 gpm) is a typical low flow condition U.S. Navy water demand that can be used for kinetic analysis. A 50 percentile flow of 301 MT/day (55 gpm) is a good estimate of the average U.S. Navy water demand at Santo Stefano. These values are summarized in table 1.1 below.

Table 1.1 – U.S. Navy Water Demand at Santo Stefano

	Flow (MT/day)	Flow (gpm)
Peak Flow (ever recorded)	873	160
High Flow (90 th percentile)	470	86
Average Flow (50 th percentile)	301	55
Low Flow (25 th percentile)	133	24

Days	January	February	March	April	May	June	July	August	September	October	November	December
1		500	382	58	49	400	402	303	396	356	411	46
2	390	449	47	94	56	428	379	271	262	290	378	70
3	350	449	116	270	49	337	328	308	383	308	516	33
4	428	385	79	324	67	412	336	311	536	411	411	41
5	400	346	93	411	14	246	285	372	433	443	396	71
6	454	400	53	422	283	292	49	363	333	426	336	86
7	407	426	48	382	93	70	77	295	383	398	401	61
8	556	383	35	407	59	91	53	382	349	376	376	55
9	345	404	52	348	66	74	50	377	389	332	341	87
10	230	405	63	349	135	72	57	378	391	346	305	65
11	465	362	38	363	60	393	52	337	405	343	612	90
12	351	327	52	363	481	417	54	452	306	295	393	95
13	389	293	23	305	437	440	71	165	460	403	393	353
14	477	406	54	419	407	430	63	315	332	400	391	457
15	375	480	50	341	305	424	53	278	365	418	464	545
16	429	332	56	304	300	461	490	410	389	332	382	581
17	360	340	53	365	377	405	465	605	428	393	377	548
18	313	407	58	311	507	544	372	402	441	382	454	461
19	397	335	51	203	372	299	385	375	401	390	495	505
20	537	358	26	442	449	354	420	349	472	445	413	479
21	357	383	47	321	438	110	382	315	354	499	481	428
22	418	467	49	341	612	61	357	343	528	458	424	463
23	560	427	57	304	400	55	313	358	381	528	599	455
24	358	371	67	303	672	47	335	358	355	539	513	379
25	130	375	66	463	600	85	333	329	340	449	449	418
26	169	409	48	167	485	30	363	206	348	504	500	423
27	107	351	59	80	540	35	345	390	323	458	459	502
28	114	437	66	106	500	54	330	377	341	439	427	535
29	88		102	87	320	54	319	380	277	419	141	512
30	113		61	86	350	50	277	514	338	411	66	540
31	314		77		312		214	503		445		474
Daily Average	346	393	69	291	316	259	331	359	381	406	410	318

Annual Daily Average = 316 MTs

Figure 1.5 – 1994 Water Demand Santo Stefano – MT

Days	January	February	March	April	May	June	July	August
1	401	461	353	292	40	79	430	77
2	413	464	382	322	320	128	363	80
3	411	513	416	424	321	65	297	79
4	492	593	342	389	284	29	331	73
5	470	594	392	319	424	30	289	82
6	500	529	344	311	260	58	311	283
7	445	489	453	330	317	51	423	332
8	399	82	408	334	310	55	464	429
9	420	71	399	305	537	69	428	873
10	374	90	604	333	323	64	257	458
11	521	61	459	321	309	26	471	340
12	435	57	333	372	322	40	334	342
13	414	73	353	360	329	70	288	353
14	477	49	338	309	264	102	344	303
15	327	37	307	304	328	68	268	328
16	407	64	329	428	258	68	161	301
17	443	43	326	316	303	40	223	333
18	294	68	330	241	330	53	263	301
19	345	296	314	312	342	34	272	284
20	414	307	255	328	319	67	79	300
21	419	377	73	322	236	68	95	344
22	437	352	68	316	228	414	110	386
23	447	342	68	217	93	321	78	356
24	490	508	220	280	48	340	67	374
25	519	406	285	300	68	260	60	354
26	496	313	252	300	58	324	73	334
27	459	324	287	301	73	414	77	355
28	344	388	315	109	39	347	29	335
29	351		157	60	31	364	101	379
30	476		235	30	52	375	50	404
31	402		226		55		71	336
Daily Average	427	284	310	296	233	147	229	320

Annual Daily Average = 281 MTs

Figure 1.6 – 1995 Water Demand Santo Stefano - MT

Considering average flow conditions from above discussion, drinking water detention times in the distribution system leading up to the 2000 MT U.S. Navy tank are just over 3.5 days. Under average flow conditions an additional 6.6 days of detention time are experienced in the U.S. Navy tank. Under low flow conditions the detention time in the U.S. Navy tank is an additional 15.0 days. These detention times are of particular interest to the discussion of disinfection and treatment options at the U.S. Naval station Santo Stefano. A disinfection residual of 0.25 mg/l free chlorine is all that remains at the U.S. Navy tank influent from the treatment at ESAF. No effort has been made by any study to measure the chlorine dioxide residual that may still be present after 3.5 days. Because of the long detention times in the U.S. Navy tank, re-disinfection is required.

2.0 Regulatory Framework

2.1 Final Governing Standards

The U.S. Navy is responsible for providing safe drinking water to all Naval and civilian personnel that are stationed on, or reside at, naval bases and ships of the U.S. Navy. For overseas installations the Department of Defense (DOD) has published an Overseas Environmental Baseline Guidance Document (OEBGD) to provide guidance to overseas activities in the development of country-specific standards for drinking water. These country-specific standards are called Final Governing Standards (FGS) and they meet the most stringent of U.S. or the host nation's standards. In 1994 the U.S. Navy developed the FGS for installations located in Italy.

A review of the complete copy of the FGS would by far be in excess of what is required to discuss distribution system management, treatment and disinfection options at the Naval Station -Santo Stefano with regard to THM reductions. What is of some concern, however, is the FGS for total trihalomethanes (TTHM's) which is 30 µg/l or 0.030 mg/l. This is less than one-third of the Environmental Protection Agencies (EPA's) regulated value for the U.S. of 0.100 mg/l.

Additionally, in order to discuss disinfection in the distribution system, the FGS requirements with regard to required distribution system disinfectant residuals must be known. As with the U.S. regulations concentration time (CT) values required for effective disinfection are calculated and required at the water treatment plant (in this case ESAF). Appendix A contains CT tables excerpted from the FGS. A disinfectant residual is required by the FGS. A minimum residual value is not specified, rather, if the value of a heterotrophic plate count (HPC) is ≤ 500 /ml then the tested water is considered to have the required residual. If more than 5% of monthly samples exceed this HPC standard in 2 consecutive months it is considered a violation of the residual standard in the FGS. At ESAF adequate

disinfection is provided so that CT requirements are met. Additionally, there are no HPC violations at the U.S. Navy tank influent. Secondary disinfection is all that is required at the U.S. Navy tank influent.

3.0 Distribution System Management

3.1 The Evolution of Distribution System Management

In the past disinfection was the main quality concern in water distribution system management. In fact, quantity not quality was stressed as the most important distribution system concern. Maintaining adequate flows, pressures and storage were often the only concern in water distribution design and certainly these were the *main* concern in water distribution system management. Systems were designed for maximum daily or hourly flow rates combined with fire demand. Storage was provided to meet fire demand and provide adequate pressures. Often there was little or no concern for water quality during the design phase of existing water distribution systems.

Certainly, an excessive detention time in water storage tanks is a large factor in declining distribution system water quality. Excessive detention times lead to the depletion of disinfectant residuals and biological re-growth. Water that has been stored for long periods of time thus has no guarantee of being delivered to the end-user in a properly disinfected manner.

With the adoption of the Surface Water Treatment Rule (SWTR), and the other amendments of the Safe Drinking Water Act (SDWA) in 1986 and 1989, the focus of water distribution management shifted to that of water quality rather than quantity. The new quality standards directed that surface water be disinfected and filtered. The maximum contaminant level (MCL) was set as well for the allowable turbidity of the filtered water. This MCL was set at 0.5 nephelometric turbidity unit (NTU). In addition, the maximum contaminant level goal (MCLG) of zero was set for *Giardia lamblia*, viruses, and *Legionella*. The disinfection was required to provide a 3-log or 99.9% inactivation of *Giardia lamblia* and a 4-log or 99.99% inactivation of viruses. The SWTR additionally required a disinfectant residual to be maintained in the water distribution system.

Legionella is a genera of mostly pathogenic bacteria, the most well-known of which is *Legionella pneumophila*. This organism causes Legionnaires' disease. Likewise, *Giardia lamblia* is a pathogenic organism that is the causative agent of diarrhea and abdominal cramps in humans. *Giardia lamblia* is a protozoon that can form a protective cyst and is thus more difficult to kill. It is found in water supplies contaminated with feces.

The significance of the above more stringent requirements is that they stressed distribution system water quality. Maintenance of a disinfection residual in the distribution system was now required by the SWTR. Additionally, the low level turbidity requirement also provided protection from pathogens in water. Turbidity is nothing more than a surrogate measure of particulate matter in water. This particulate matter, although not necessarily itself harmful to human health, can harbor and protect pathogenic organisms that may be attached or entrained in them.

Some of the other regulations of the SDWA that were promulgated in 1986 and are driving significant change in water distribution management are the following:

- Total Coliform Rule (TCR)
- Lead and Copper Rule

As a result of these more stringent regulations it is no longer good enough to meet treatment requirements for potable water at the plant only. The entire distribution system must be managed properly to provide safe water to the end-user at the "tap".

3.2 Multiple Barrier Approach to Microbial Control

In order to meet the new quality standards brought on by the amendments to the SDWA – which form a significant portion of the FGS in Italy, complete distribution system management must be performed. The solution to violations of the SDWA and its amendments lies in the management of all phases of the water distribution system.

The above concept is referred to as a multiple barrier approach to microbial control (Knight, 1996). Stated simply, in order to deliver safe drinking water to the end user the elements of importance are not just treatment and disinfection at the water treatment plant (WTP). Additional concerns that must be considered to meet the new regulations are the quality of the headwater or source and microbial control in the distribution system. This concept is illustrated in the following Figure 3.1. This concept holds for all water quality constituents. It is through a review of all phases of the water treatment and distribution system that possible solutions to water treatment problems can be obtained.

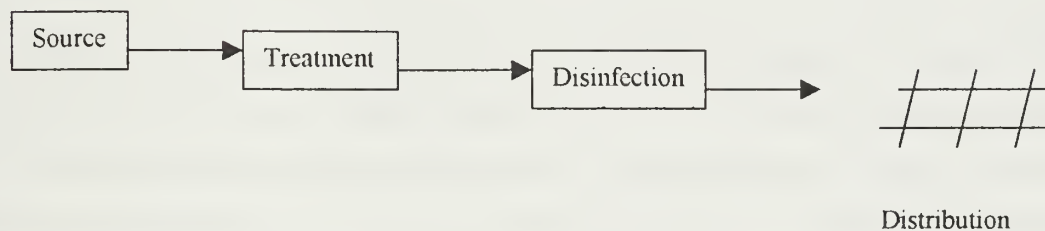


Figure 3.1 – Multiple Barrier Approach to Microbial Control

Clearly then, in determining possible solutions for various water quality violations in a distribution system a review of the management of all four of these barriers must be accomplished. For instance, when looking at a violation of the Total Coliform Rule (TCR) it is not enough to simply verify that there is proper disinfection at the plant. Perhaps detention times in the distribution system at various points are too extensive and chlorine booster stations are required. Other possible solutions could be modifications to storage in the distribution system or to treatment and disinfection at the plant. Even modifications to point source discharge permits at the headwater could be a possible solution. How these various approaches could be used will become clearer with further discussions in the following sections.

3.3 Trihalomethanes (THM's) Defined

In order to partake further discussions on control of THM's by distribution system management, a more in depth knowledge of what THM's are and what causes them is required. As previously stated, when water is disinfected by use of chlorine the regulated THM's are formed. Generally speaking, THM's are disinfectant by products (DBP's) formed by the use of chlorine to disinfect drinking water containing organic matter. When water containing organic humic and fulvic acids is disinfected with chlorine, the oxidation of these acids by chlorine results in the formation of THM's. These DBP's are regulated since they are suspected human carcinogens. They are currently the only group of DBP's that are regulated.

THM's can be further defined as a group of halogenated organic compounds. When chlorine reacts with the natural organic matter (NOM), and bromide (Br) to varying degrees, in water these halogenated compounds are formed. A listing of these compounds and their chemical symbols is shown in Table 3.1. Collectively, these four compounds are referred to as total trihalomethanes (TTHM's). It is this total value that is regulated by the U.S. EPA at a value not to exceed (MCL) 100 µg/l, and by the FGS in Italy at an MCL of 30 µg/l.

TRIHALOMETHANES

<i>Chemical Symbol</i>	<i>Chemical Name</i>
CHCl ₃	Chloroform
CHCl ₂ Br	Bromodichloromethane
CHBr ₂ Cl	Chlorodibromomethane
CHBr ₃	Bromoform

Table 3.1

3.4 THM Reductions

As previously stated there are four barriers to microbial control in water distribution systems. A review of each barrier must be accomplished if one is seeking solutions for water quality concerns at a given location. In the following paragraphs we will discuss possible solution scenarios for the THM problem at Santo Stefano within reference to: source, treatment, disinfection, and distribution system.

3.4.1 Source Water/ Source Water Protection Issues at Santo Stefano

First we will discuss alternate solution scenarios that could arise from the *protection* of the source water. Problems with the source water that can cause water quality issues in a water distribution system can vary. Microbial and chemical contamination of surface waters or ground waters influenced by surface waters is always a concern. Locations of landfills, septic tanks, farmlands etc. become a possible concern for this matter. The SWTR takes care of much of the microbial concerns, but for an extra level of protection the proximity to these items is a concern. Farmlands in particular that are fertilized with animal waste can create a large influx of microorganisms including cyst forming *Giardia lamblia*. This, however, is not the problem of concern in this study; THM's are.

An additional source water concern is the influx of TOC. If the source water is surrounded by agricultural drainage, particularly from tracts of land that are high in peat soil, it could be a major source of TOC. This can cause a large increase in the TTHMFP of the water. Additionally, wetlands can also contribute significantly to the introduction of TOC. Protecting the source water from such influxes is becoming a large issue with the high cost of removing these DBP precursors once they are in the source water. Part of the solution to this problem is being ever diligent in the enforcement of erosion control measures to limit non-point source discharges. Point source discharges and other sources of dissolved TOC are of even greater concern. There is, however, no definitive single solution for this problem. Since the Italians perform the primary water treatment, and the U.S. Navy currently has no

knowledge of the headwater TOC concentration, no possible source water protection scenarios will be discussed in this report.

A source water concern not involving protection, however, which warrants some discussion is high bromide concentration. This is often caused by water with a great amount of saltwater intrusion. Lakes, however, with no saltwater intrusion can contain a high level of bromide. Symons et. al. in “Precursor Control in Waters Containing Bromide” discussed a reservoir on the Colorado river (Lake Austin) that was partially fed by groundwater passing through fractured limestone. The bromide concentration in excess of 0.5 mg/l was attributed to this ground water infiltration (Symons et al., 1994). The reason that high bromide concentrations are a concern is that they increase the TTHM formation potential (TTHMFP) of the water. Bromide and NOM (measured as total organic carbon, TOC) are the two constituents that determine TTHMFP and the species of THM produced (see Table 3.1). Other conditions such as the UV absorption properties of the TOC, time, temperature, pH, and chlorine dose influence the reaction between chlorine, bromide, and TOC. From the perspective of the source water characteristics it is the NOM concentration and characteristics, and the concentration of bromide that directly influences the THMFP of a sample of water at a given temperature and pH.

Although an exact bromide concentration was not available for the source water that supplies Santo Stefano, the distribution of the species of THM's made it apparent that there was significant bromide in the water; at low bromide concentrations chloroform dominates all brominated species. The following table shows the distribution of the THM species produced by a 3-mg/l dose of chlorine to the water at the Santo Stefano site after 14 days of contact time (Malcolm Pirnie, 1996). It is important to note that this distribution of THM species was obtained by chlorination of U.S. Navy tank influent water at Santo Stefano. Santo Stefano water under well-controlled laboratory conditions produced the speciation shown in Table 3.2 after 14 days. The high levels of chlorodibromomethane and bromoform (total of almost 64%) made it evident that there was a high level of bromide in the water. An

Table 3.2 – THM production after 14 days with 3-mg/l Cl₂ dose (Laboratory)

SPECIES OF THM's (μg/l)

CHCl ₃	11
CHCl ₂ Br	28
CHBr ₂ Cl	40
CHBr ₃	24
TTHMFP	103

approximate value of the bromide concentration could be obtained, however, from the observed THMFP in the laboratory. To do this would require modeling the water in terms of the variables that affect THMFP.

To model the THMFP of Santo Stefano water the following equation (Eqn 3.1) from Amy, Chadik and Chowdhury (1987) was chosen. This model was chosen because of the extensive database that it was based on. In creation of this database the chlorination of 13 different natural bodies of water was studied that varied significantly in all parameters that affect THM production. The range of parameters in the tested waters is shown in Table 3.3.

$$\text{(Eqn 3.1) THM} = 0.00309[(\text{TOC})(\text{UV-254})]^{0.440}(\text{Cl}_2)^{0.409}(\text{t})^{1.06}(\text{pH}-2.6)^{0.715}(\text{Br}+1)^{0.036}$$

Where:

- THM = TTHM concentration in [μmole/L]
- TOC = total organic carbon concentration in [mg/L]
- UV-254 = absorbance of 254 nm wavelength UV light in [cm⁻¹]
- Cl₂ = chlorine dose in [mg/L]
- t = reaction time in [hours]
- T = temperature in [°C]
- Br = bromide concentration in [mg/l]

To convert the results from Eqn. 3.1 to μg/L the following equation from Amy, Chadik and Chowdhury was utilized.

(Eqn 3.2) $AMW = 105.3(Br + 1)^{0.48}(UV-254)^{-0.089}$

Where: AMW = the average molecular weight of the THM species formed

By multiplying the results of the two equations together the TTHM formation can be determined in $\mu\text{g/L}$.

Table 3.3

Range of Values Tested in Formation of THM Model

Number of natural bodies of water	13
Number of data points	1090
TOC (mg/l)	3.0 – 13.8
UV-254 (cm^{-1})	0.063 – 0.489
Chlorine dose (mg/L)	1.5 – 69
Bromide concentration (mg/L)	0.01 – 1.245
pH	4.6 – 9.8
Temperature ($^{\circ}\text{C}$)	10 – 30
Time (hours)	0.1 – 168

In order to approximate the concentration of bromide it was necessary to fit a curve that predicted the values of the THMFP that were observed in the laboratory. Table 3.4 gives the laboratory results for THMFP as a function of time that were measured in the laboratory by chlorination of Santo Stefano U.S. Navy tank influent. Table 3.5 gives the model-predicted values for TTHMFP at bromide concentrations of 0.0 mg/L and 0.3 mg/L, using the following measured and approximated values:

- TOC = 2 mg/l
- Cl_2 = 3 mg/l
- T = 22 $^{\circ}\text{C}$
- pH = 7.8
- UV-254 = 0.040 cm^{-1}

As can be seen from the data for the 1, 2, and 14-day values for the TTHMFP, there was good agreement between the model prediction at 0.3 mg/l and the actual laboratory data. How closely the data correlated can be more clearly seen in Figure 3.2. Figure 3.2 shows that only the 3-day value for the laboratory data varied to any significant degree. Moreover, this data point did not appear to fit the laboratory data curve either. Since the 14 day prediction showed 0.08% error, the correlation was considered to be acceptable, and the approximate value of the bromide concentration was assumed to be 0.3 mg/l.

Table 3.4

TTHMFP AT SANTO STEFANO WITH A 3 mg/l Cl_2 DOSE (LABORATORY)

<i>Contact Time (days)</i>	<i>TTHMFP ($\mu\text{g L}$)</i>
0	12
1	50
2	61
3	77
14	103

Table 3.5

TTHMFP PREDICTED BY MODEL

<i>Contact Time (days)</i>	<i>TTHMFP ($\mu\text{g L}$)</i>	
	<i>Br conc. = 0.0 mg l</i>	<i>Br conc. = 0.3 mg l</i>
1	45	51
2	54	61
4	64	74
6	72	82
8	78	89
10	82	94
12	86	99
14	90	103
16	93	107

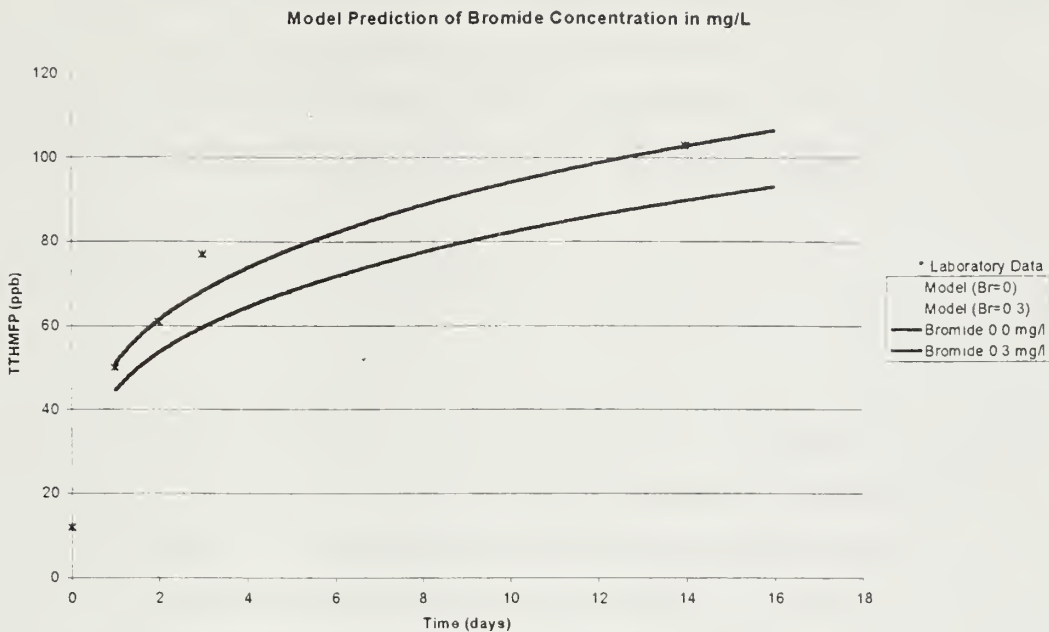


Figure 3.2

The above model has been shown to closely approximate the field data. This fitted model can clearly be valuable in determining how varying certain parameters such as pH, temperature, contact time, and chlorine dose might affect the TTHMFP of the Santo Stefano water. This will be expounded further in later sections, but for now it has just been utilized to determine the approximate bromide concentration of Santo Stefano water since this information was not directly available.

Unfortunately, there are few options available to remove bromide from the Liscia Reservoir-source water. There is even less one can do to protect the source water from the natural occurrence of bromide that is clearly experienced at Santo Stefano. If the source of the bromide were saltwater intrusion, perhaps drawing water further upstream would be a solution. This would be a costly option, however, and likely impractical to offset the minor increase in THMFP from the bromide's presence.

In conclusion controlling the influx of TOC's into the source water is one method of reducing the THMFP of the Santo Stefano water. With no knowledge of the source water

TOC concentration, and since the Italians control the primary water treatment, no effort will be made to address possible solution scenarios involving the reduction of TOC at the source water. In addition, a significant concentration of bromide is likely present in the source water. The fitted TTHMFP model will be used later to determine how varying pH, contact time, and chlorine dose might affect the TTHMFP of the Santo Stefano water.

3.4.2 Water Treatment Issues at Santo Stefano

As stated previously, THM's are formed as a by-product of the reaction of chlorine with organic material in the water. One *treatment* option to solve the problem of high levels of THM's at Santo Stefano would be the removal of the organic precursors before disinfection. These precursors could be assumed to be completely in the dissolved fraction based on the treatment process at ESAF (microscreen, alum coagulation, sand filtration, GAC filter). In order to remove these dissolved organics there are several options. The ones to be discussed in this report are:

- Carbon Adsorption
- Reverse Osmosis/ Ultrafiltration
- Advanced Oxidative Procedures.

Reverse Osmosis is the transport of a solvent from a dilute solution to a concentrated solution across a semipermeable membrane that impedes the passage of the solute but allows the solvent to flow. This process would generate a significant waste stream of concentrated reject water. Since water capacity is an additional problem at Santo Stefano, however, this would not be a good treatment option. During the peak demand times in the summers, low pressures and sometimes a lack of water supply are experienced – reverse osmosis would only add to the water capacity problem.

Advanced oxidative procedures (AOP's) is a term that first appeared in the literature

in 1987 (Symons and Worley, 1995). It refers to oxidation processes that depend on the creation of the hydroxyl free radical ($\cdot\text{OH}$) as the oxidant. The hydroxyl free radical is a very strong oxidant, and hence it destroys the organic material it comes in contact with. Various combinations of oxidants have been used to perform as AOP's. To list a few, combinations such as ozone (O_3) and ultraviolet radiation (UV), ozone and hydrogen peroxide (H_2O_2), and UV and hydrogen peroxide have all been tested.

The advantage of the use of AOP's is that they can completely destroy a significant amount of the organic matter in the water - removing would be THM precursors. The end products to the AOP's are carbon dioxide and water. Processes such as granular activated carbon (GAC) adsorption, which will be discussed shortly, require reprocessing of the carbon after the water has been treated. This can be an expensive and complicated proposition. Clark and Lykins in *Granular Activated Carbon: Design, Operation and Cost* state that smaller systems (≤ 10 mgd) experience significantly higher unit costs than larger systems (Clark and Lykins, 1989). Extrapolating a cost for 0.08 mgd (Santo Stefano average flow) from onsite infrared reactivation (at 3mgd) in the aforementioned text results in a cost of approximately \$8,600/year. Significantly higher unit costs would be involved for our low flow situation, however. Additionally, virgin carbon replacement is an even more expensive option.

A disadvantage in AOP's is that there is not nearly the performance track record and pre-engineered equipment available for many of these processes as there is for processes such as GAC adsorption. Surely there is a possible solution to the THM formation problem at Santo Stefano that could be derived from the use of AOP procedures, but they are highly experimental - and some of them are costly. In addition, the design for implementation of one of these processes would be a lengthy enough proposition to warrant publishing a separate report. For the purposes of this report, the most likely alternative AOP encountered during my research was the H_2O_2 – UV process studied by Symons and Worley (1995). Hydrogen peroxide can be obtained in a 30 percent solution, which makes this process cheaper and easier than one that involves the use of ozone. The cost for design and implementation of this process might prove to be prohibitive, however, the operating costs

would most likely be cheaper than carbon adsorption due to the added cost of regenerating carbon.

Adsorption is a process comprising of the mass transfer of a substance in the liquid phase to the surface of a solid (the adsorbent) where it is bound by chemical or physical forces (Cornwell and Davis, 1991). In the case of GAC adsorption, the activated carbon is the adsorbent. This process has been shown to be effective in the removal of the THM precursor organics. The greater percentage of THM precursor removal required the more frequent the replacement/ reactivation of the activated carbon. Since there is enough pre-engineered equipment available this option becomes the best treatment option available for Santo Stefano.

In conclusion, GAC adsorption becomes the most likely treatment option for Santo Stefano. A preliminary design will be discussed outlining a solution utilizing GAC adsorption in Section 5.0 of this report.

3.4.3 Water Disinfection Issues at Santo Stefano

There are several disinfection options for reducing the formation of THM's at Santo Stefano. All of them stem from utilizing alternate disinfectants for microbial control than free chlorine (Cl_2). If free chlorine is not used, or it's contact time with the water to be disinfected is limited, then the THM formation can be either eliminated or controlled respectively.

The most commonly utilized disinfectant for water treatment is free chlorine. The other commonly utilized chemical disinfectants for water, and thus the ones that will be discussed here, are:

- Chloramines
- Chlorine Dioxide (ClO_2)
- Ozone (O_3)

Through the use of various combinations of these disinfectants, and/or various application points, these disinfectants could be utilized to provide the disinfection residual required at Santo Stefano, without exceeding the FGS standard of 30 ppb for THM's. A complete discussion of disinfection theory with respect to each of these disinfectants and possible solution scenarios will be discussed in section 4.0 of this report.

3.4.4 Water Distribution System Management Issues at Santo Stefano

Largely, water distribution system management issues deal with protecting the water as it is transported to the user from microbial or other contamination. Programs and monitoring efforts that should be established and performed related to this are:

- Cross-connection prevention programs
- Flushing programs
- Maintaining adequate pressures (leak detection program)
- Valve exercising programs
- Maintaining disinfectant residuals

A cross connection is any physical connection between a potable water system and a non-potable water system. The non-potable water systems can be anything from fire sprinkler system water to steam generator water. If a pressure differential develops which is favorable for the flow of water from the non-potable system to the potable water system, foreign substances can be introduced into the water distribution system. In order to prevent this, backflow preventers must be installed at these locations. Although a cross connection program is required to ensure that stagnant or otherwise unsafe water is not delivered to the end-user, there are likely minimal THM ramifications from a possible cross connect.

Similarly, flushing programs, maintaining adequate pressures, and valve exercising programs all deal at least in part with the delivery of properly disinfected water to the end user. Flushing programs to remove stagnant water, maintaining adequate pressures to prevent backflow at cross connections, and valve exercising programs to ensure isolation from contamination during repairs surely are beneficial to water quality. The impacts on THM formation, however, are small if existent at all.

The distribution system management issue that is at the heart of the problem at Santo Stefano, however, is the maintenance of a disinfectant residual. In order to give added protection in the incidence of failures of the above programs, a disinfectant residual must be maintained in the water distribution system. If a more persistent disinfectant residual were supplied at the main water treatment plant (ESAF), the re-chlorination that creates the THM's currently occurring at Santo Stefano might not be necessary. Additionally, average flow conditions of 301 MT/day provide a detention time of over 6 days in the 2000 MT U.S. Navy storage tank (Figure 1.4). Long detention times (typically greater than 3 days) make maintenance of a disinfectant residual even more difficult without the production of THM's. Alternate disinfectants for the management of a residual, without the significant THM production, will be discussed in the next section. Allowable detention times will be discussed throughout as possible solution scenarios are discussed.

4.0 The Disinfection Approach

4.1 Disinfection Theory

We have previously stated that disinfection is required by the SDWA amendments that are part of the FGS in Italy. It was also stated that the concentration and duration of contact required for primary disinfection is governed by concentration time (CT) values to provide a 3-log inactivation of *Giardia lamblia* (this is a more stringent requirement than the 4-log inactivation of viruses which is also required). Additionally, we stated that a disinfectant residual was required to be present in the distribution system. In the FGS an HPC of $\leq 500/\text{ml}$ is used as evidence that a viable disinfectant residual is present in the water. But what is the theory behind disinfection? How safe is the disinfection supposed to make the water? Is it sterilized?

To answer these questions, the theory behind disinfection is the removal or inactivation of pathogenic organisms. Disinfected water is not sterilized. It is not the purpose of disinfection to kill all living organisms in the water supply. There is no need for the added expense of sterilizing the water supply from all harmless organisms. A disinfectant, however, must be able to kill or inactivate *pathogenic* bacteria, viruses, and amebic cysts. Since the water in the distribution system is not sterile and there are food sources (NOM) in the supply as well; a biofilm (layer of living organisms) will in fact be present on the pipe walls. A distribution disinfectant residual is required to provide protection against recontamination and control biofilm growth. This recontamination can come from:

- low pressures and backsiphonage of sewage
- other non-potable water cross-connections
- the atmosphere at air-water interfaces in tanks
- water line breaks, service, or construction activities

- Re-suspension of biofilm growth in pipes due to hydraulic disturbances

4.2 Alternate Disinfectants

Utilizing the theory behind disinfection it is now possible to discuss the five main disinfectants relative to performance as primary and/or secondary disinfectants. As previously listed the main disinfectants to be discussed are:

- Chlorine (Cl_2)
- Chloramines
- Ozone (O_3)
- Chlorine Dioxide (ClO_2)

4.2.1 Chlorine (Cl_2)

As has been previously alluded to, chlorine is the most commonly utilized disinfectant. So commonly utilized is chlorine that the terms chlorination and disinfection have almost become synonymous. When chlorine is utilized in water treatment there are three important reactions in which chlorine participates (Connell, 1996). These three reactions are oxidation, substitution, and disinfection.

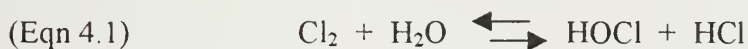
Oxidation is a reaction characterized by the release of electrons. Chlorine acts as an *oxidizing agent* in these oxidation reactions and is said to be reduced when it accepts electrons. Although chlorine oxidizes inorganic compounds and it is of benefit from a water treatment standpoint, it is of little significance to the THM problems at Santo Stefano. The other oxidation reaction, however, with organic material is the reaction that has previously been explained to cause the formation of the regulated THM's. Substitution reactions deal with the replacement of an element or a portion of a chemical molecule or organic compound with an ion, in this case the chloride ion (Cl^-). This is important in the formation of chloramines and will be elaborated on later with their discussion. Disinfection is the destruction or inactivation of pathogenic organisms in the water. *Disinfection will be the*

underlying element of discussion here and it is not always correlated directly with oxidation. It must be made clear that for chlorine, oxidation is not the avenue to disinfection that it may be for other disinfectants.

Application of chlorine is primarily accomplished in two forms:

- Elemental chlorine gas
- Hypochlorite compounds (solid or liquid)

Elemental chlorine boils at -30.1°F (-34.5°C) at the standard pressure of 1 atmosphere (atm). It is stored and shipped under pressure as a liquefied gas. When added to water the molecules of chlorine react with water in a reaction called hydrolysis to form hypochlorous acid (HOCl) and hydrochloric acid (HCl) by the following reaction.

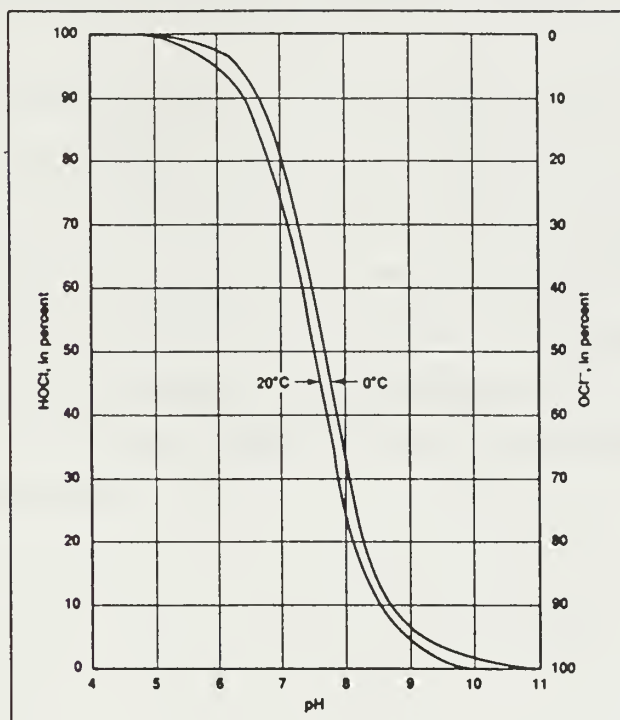


Of the two products created, the HOCl is the important product from a disinfection standpoint. This hypochlorous acid then dissociates into two components by the following reversible reaction.



The avenue of disinfection for chlorine is through the penetration of the cell wall of the pathogenic organism by the hypochlorous acid (HOCl) or the hypochlorite ion (OCl^-) (Connell, 1996). The hypochlorous acid or hypochlorite ion then can interrupt the various life processes of the organism or alter the enzymes that catalyze these processes. Life processes that may be disrupted include food ingestion, food absorption, waste discharge, mobility, and ability to replicate. Since most organisms have a negatively charged outer cell wall, the charge of the disinfectant attempting to penetrate the cell wall becomes important. The negatively charged OCl^- has a much harder time penetrating the negatively charged cell wall than the neutrally charged HOCl. For this reason the most effective disinfectant created

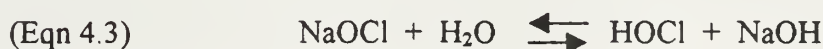
by the introduction of chlorine to water is the hypochlorous acid. It follows that high pH levels would force the reaction in Eqn. 4.2 to the right because of the demand for the hydronium ion (H^+) caused by the base. Figure 4-1 shows the relative concentrations of HOCl and OCl^- at various pH's. It is clear to see why, from this figure, the most effective disinfection by chlorine occurs at $pH < 7.5$.



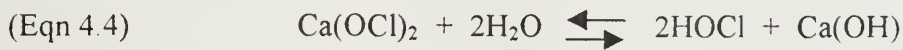
Source: AWWA (1973).

Figure 4.1 – pH affect on hypochlorous acid/ hypochlorite ion distribution

The above Eqn 4.1 described the reaction that takes place when chlorine gas is added to water to obtain hypochlorous acid. Hypochlorite compounds can also be added to water to produce the HOCl. The most common hypochlorite compound utilized is sodium hypochlorite ($NaOCl$). $NaOCl$ comes in solutions that have concentrations of up to 15% hypochlorite and are widely used. When $NaOCl$ is added to water, HOCl is formed by the following reaction.



A far less utilized hypochlorite compound that can be added to water to produce hypochlorous acid is calcium hypochlorite ($\text{Ca}(\text{OCl})_2$). Calcium hypochlorite products contain approximately 70% hypochlorite and are available in tablet or granular forms rather than solutions. When $\text{Ca}(\text{OCl})_2$ is added to water, HOCl is formed by the following reaction.



The advantages to the use of chlorine as a disinfectant are well established. It provides a stable free chlorine residual of HOCl or OCl^- when dosed at a level to exceed the initial chlorine demand. The chlorine residual will last in a distribution system that is not too large. If detention times exceed 2 to 3 days rechlorination in the distribution system will likely be required. The initial chlorine demand is defined as the initial amount of chlorine that is utilized in oxidizing various organic and inorganic materials as well as the initial requirement for disinfection. The chlorine dose must always equal the chlorine demand plus the desired residual concentration.

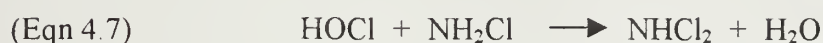
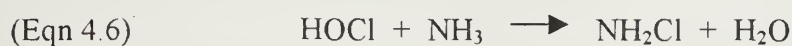
(Eqn 4.5)
$$\text{Chlorine Dose} = \text{Chlorine Demand} + \text{Chlorine Residual}$$

When dosed at the proper levels to provide the CT required in the tables in appendix A it is an effective primary disinfectant as well. From a cost standpoint disinfection with chlorine is very cheap and is a minimal fraction of overall water treatment costs. Costs of course will increase if rechlorination stations that have to be monitored and maintained are required in a distribution system.

The disadvantages to chlorine disinfection are also fairly clear. If humic and fulvic acids are in large enough concentrations in the water, the regulated THM's (suspected carcinogen) are produced. Other disinfection by-products are also produced that shortly will be regulated such as haloacetic acids (HAA's). In addition, there is a limit beyond which the disinfectant residual will not last. If this is the case, rechlorination stations are required which increases the cost of the disinfection practice.

4.2.2 Chloramines

Chloramines are the reaction products of the combination of hypochlorous acid and ammonia (NH₃). These reactions are shown in simplified form in the following equations.

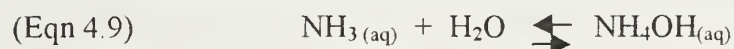


These reactions are termed substitution reactions because the chlorine atom substitutes for the hydrogen atom in the ammonia molecule. The product in Eqn 4.6 is called monochloramine, in Eqn 4.7 dichloramine, and in Eqn 4.8 trichloramine or nitrogen trichloride.

Application of ammonia is accomplished in two general forms:

- Molecular ammonia gas
- Solutions of ammonia or ammonia salts

Molecular ammonia boils at -28.2°F (-33.4°C) at the standard pressure of 1 atm. It is stored and shipped under pressure as a liquefied gas. When added to water the molecules of ammonia participate in the following reversible reaction.



The aqueous ammonia then participates in the reactions shown in equations 4.6, 4.7, and 4.8 to form the chloramines.

Rather than feeding ammonia gas through an ammonia gas feeder to form the aqueous ammonia, it is also available pre-mixed in an aqueous ammonia form. These solutions of ammonia are the most widely used form. The aqueous ammonia, instead of being formed in the venturi of a gas feeder, is immediately available in these solutions to participate in the reactions to form chloramines.

Additionally, ammonia is available in solutions of ammonia salts. These are less commonly utilized than the solutions of ammonia. The most common solution of ammonia salt is ammonium sulfate ((NH₄)₂SO₄). The ammonium sulfates and other ammonium salts produce ammonium hydroxide (NH₄OH) in reactions similar to the following.



The resultant ammonium hydroxide then produces aqueous ammonia by the reaction shown in Eqn 4.9. The aqueous ammonia is now available to form chloramines.

It should be noted that the valence charge of the chloride ion is +1 in the chloramine compounds just as it had been in the hypochlorite ion and hypochlorous acid. For this reason the chlorine is still available as an oxidizing and disinfection agent. Since the chlorine has been combined, however, with nitrogen and hydrogen in the ammonia molecule, it is no longer as readily available for oxidation and disinfection. The chemical bonds holding chlorine in the molecule alter the availability, speed, and type of chemical reactions in which chlorine can be involved (Connell, 1996).

The avenue for disinfection remains the same for chloramines as it was for chlorine. The chloramine compounds are neutrally charged and may enter pathogenic organisms through the negatively charged cell wall in the same manner that hypochlorous acid enters with the use of free chlorine.

The forms of chloramines created, at this point, become important in water disinfection and quality (including aesthetics). The di- and trichloramine have much lower

odor and taste thresholds than monochloramine and free chloramine. For this reason it is desired to form monochloramine and not di- and trichloramines. At a given temperature, the species of chloramines formed are a function of pH and chlorine-to-ammonia ratio. The various species of chloramines that are created as a function of pH are shown in figure 4.2 below.

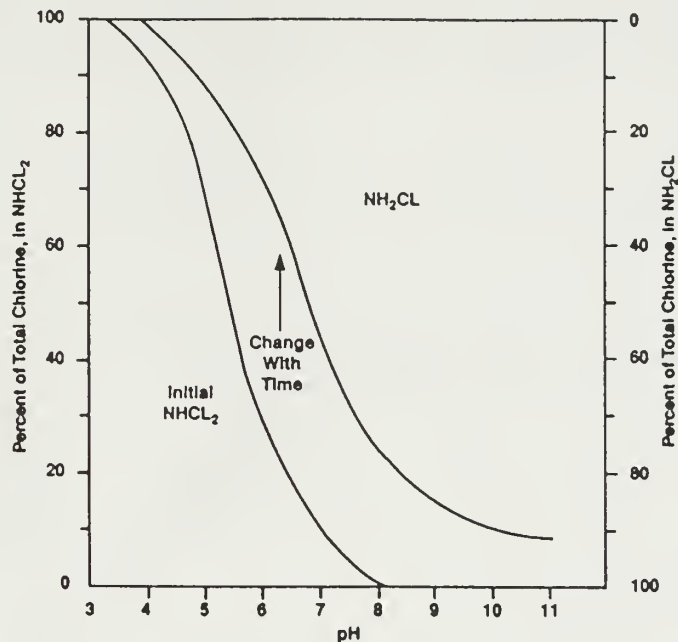


Figure 4.2 – pH affect on mono- and dichloramine distribution

It is clear to see from this figure why it has been found that for optimizing chloramine treatment a pH in the range of 7.5 to 9 has been found as the ideal range (Kirmeyer et al., 1993).

A graphical view of how the chlorine residual varies with increasing chlorine dosage in a water containing ammonia will help to explain how the chlorine: ammonia-nitrogen ratio (Cl_2 : $\text{NH}_3\text{-N}$) affects the species of chloramine produced. This graphical view is called the breakpoint curve and is common in any text that discusses chloramines. It is shown in figure 4.3 on the following page. In this breakpoint curve zone 1 illustrates the initial chlorine demand exerted by the water. In zone 2 any additional chlorine dose in the presence of ammonia will be measured as combined chlorine (another term for chloramines). If the

water were free from any and all chlorine demanding substances the zone 2 line would follow the zero demand line. With increasing $\text{Cl}_2:\text{NH}_3\text{-N}$ ratio in zones 3 and 4 the chlorine begins to consume the chloramine residuals. This reaction, in the pH range of 7 to 8, takes place stoichiometrically at a $\text{Cl}_2:\text{NH}_3\text{-N}$ ratio of 7.6:1. This point is at the peak in zone 3 of Figure 4.3. The breakpoint is said to have been reached at the bottom of the curve between zones 4 and 5. In practice this is said to have been reached at 10 parts chlorine to 1 part ammonia nitrogen. Any additional chlorine dose will be present as a free chlorine residual in zone 5.

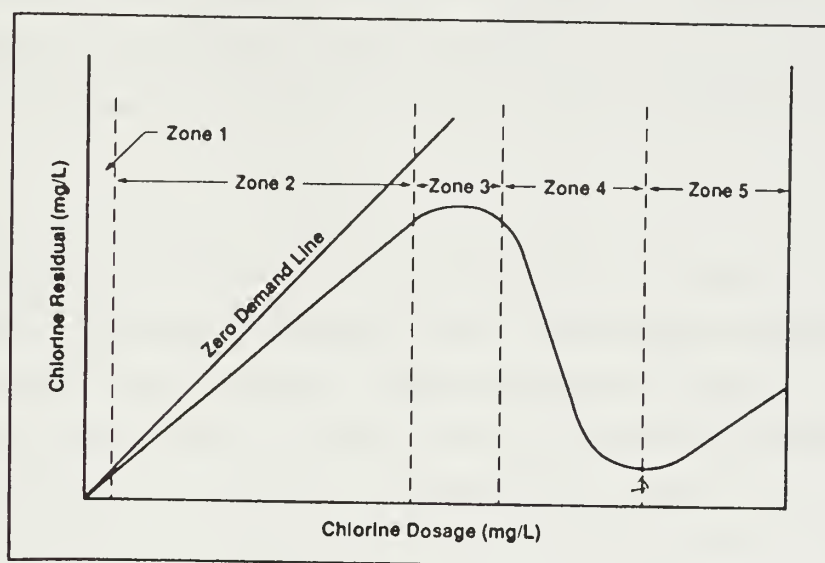


Figure 4.3 – Breakpoint curve

The chlorine- ammonia ratio dictates not only what species of chloramines are formed but also whether they will be present at all. It has been determined that for optimum monochloramine formation the $\text{Cl}_2:\text{NH}_3\text{-N}$ should generally be maintained in the 3:1 to 5:1 range (Kirmeyer et al., 22).

The advantages to using monochloramine are well established. Combined chlorines are a less aggressive disinfectant, are more persistent in the water distribution system, and react more slowly with oxidizable materials and bacteria in water than free chlorine. For this reason, once combined chlorines are formed THM formation ceases. Additionally, since

they are less aggressive they last longer in the distribution system than free chlorine and make an excellent secondary disinfectant. This property often allows their use in long distribution systems with long detention times, without the need for rechlorination stations that likely would be required with free chlorine. Studies have been performed showing that combined chlorines can out perform free chlorine on long distribution systems. Neden et al. (1992) found that the use of monochloramine not only improved the taste and odor of the supplied water, but also provided better protection against bacterial regrowth measured by HPC. Finally, disinfection with chloramines is of comparable cost to disinfection with chlorine. Further, in long distribution systems that use chlorine as a disinfectant re-chlorination stations are often required. Switching to chloramines in long distribution systems is often much cheaper as a result of not having to operate and maintain these stations.

The disadvantages of combined chlorines start with the long contact time required if they are to be utilized as a primary disinfectant. There are also some unregulated DBP's that are still formed with the use of chloramines. Additionally, if ammonia dosages are not controlled properly excess ammonia can stimulate the growth of nitrifying bacteria. Further, if the chlorine to ammonia ratio is not controlled properly taste and odor can be a problem. And finally, deterioration of elastomers is greater with chloramines than with free chlorine, particularly in warmer climates (Kirmeyer et al., 1993). This list of disadvantages, however, mostly vanishes with proper management of a water distribution system.

One additional concern in some water distribution systems is that chloramines must be removed from waters that are being used in kidney dialysis units. There are effective procedures available to accomplish this; but before a utility can convert to the use of chloramines, the hospitals must be notified and procedures put in place if necessary. In water systems that have kidney dialysis units, this would be an additional cost consideration for switching to chloramines.

4.2.3 Ozone (O₃)

Ozone is a strong oxidizing gas that oxidizes most organic and inorganic molecules in water. Unlike chlorine, ozone does not react with water to form a separate disinfecting species. The mode of action for ozone, rather, is simply destruction by oxidation.

Pathogenic organisms as well as trace concentrations of organic material and inorganic molecules are simply destroyed by oxidation. The ozone decomposes in water to produce oxygen and hydroxyl free radicals in minutes. The hydroxyl free radicals ($\cdot\text{OH}$) themselves are strong oxidizing agents.

Ozone (O_3), a molecule containing 3 atoms of oxygen, is generally formed by an apparatus called a discharge electrode. Generation of ozone must be accomplished on site due to its rapid decomposition. The generated ozone gas is then diffused into the water to be disinfected.

The advantages of using ozone are the following:

- No THM formation.
- Very strong primary disinfectant that requires less contact time and lower dose than hypochlorous acid to kill pathogenic organisms.
- Can sometimes destroy trace organics, and result in less THMFP in treated water.
- Can under certain conditions destabilize colloids to reduce turbidity

The disadvantages of using ozone are the following:

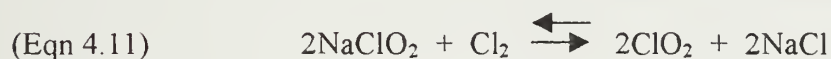
- Decays back to diatomic oxygen in minutes and therefore provides no disinfectant residual.
- Formation of other DBP's soon to be regulated. Bromate (BrO_3^-) is formed in waters containing bromide. Additionally, aldehydes are formed as DBP's.
- High cost of generation. Because of this it is rarely applied for disinfection purposes alone. It is usually used for disinfection and one of the following:
 - taste and odor control
 - oxidation of THM precursors
 - oxidation of synthetic organic chemicals

There are some procedures to control the formation of bromate. Diffusing ozone into

the water at a lower pH reduces the bromate formation. In addition, ammonia addition to the water to be treated with ozone can reduce the bromate formation. A combination of adjusting pH and ammonia addition can optimize the bromate formation with respect to bromate and TTHM formation (Symons et al., 1995). Whether this optimization is significant enough depends on the amount of Bromide and THM precursors in the water.

4.2.4 Chlorine Dioxide (ClO₂)

Chlorine dioxide is produced on site at water treatment facilities by the combination of a solution containing sodium chlorite and chlorine gas in controlled proportions. When the feed rates of these two chemicals are optimized, greater than 95 percent of the available chlorite ion reacts to produce chlorine dioxide. Chlorine dioxide is thus produced by the following equation.



Chlorine dioxide (ClO₂) is the disinfecting species. The chlorine dioxide is present as a dissolved gas in the pH range of drinking water. The chlorine atom in the ClO₂ molecule, however, has a valence of +4 and is a stronger oxidizing agent than hypochlorous acid (HOCl). The neutral charge of the ClO₂ molecule still allows for easy infiltration of the negatively charged cell wall on pathogenic organisms.

The fact that chlorine dioxide is a much stronger oxidant than hypochlorous acid directly translates to some advantages and disadvantages. With such a strong oxidation potential the chlorine dioxide molecule will react quickly in oxidizing reactions with various substances and will not maintain a residual for as long as free chlorine. The advantage of the stronger oxidation potential, however, is the much faster disinfection provided. This can clearly be seen from the CT tables in appendix A.

Chlorine dioxide has one additional advantage. It does not react with organic precursors to form THM's. Due to some inefficiencies, however, in the formation of chlorine dioxide (see Eqn. 4.11 above) some free chlorine will usually be present in the chlorine dioxide applied to the water. This free chlorine in the feed solution can form a minimal amount of THM's. In addition, chlorine dioxide does form two byproducts – the chlorite ion (ClO_2^-) and to some extent the chlorate ion (ClO_3^-). An MCL of 1 mg/l has been proposed by the U.S. EPA under stage 1 of the Disinfectants/Disinfection-By-Products Rule (D/DBP) for the chlorite ion due to health concerns (Gregory, 1998). The one-electron oxidative pathway forms the chlorite ion when ClO_2 reacts with various substances (i.e. dissolved metals) in the water. This reaction is shown in the following equation.



Gregory (1998) determined that chlorite concentrations in the distribution system at Fort Collins, Colorado were 65-70% of the applied chlorine dioxide dose. Chlorite concentrations in various distribution systems can range anywhere from 60-80% of the chlorine dioxide dose. The chlorate ion production is extremely minimal and is most likely formed in the chlorine dioxide generation process.

One additional disadvantage of chlorine dioxide is that the high cost of sodium chlorite makes ClO_2 disinfection more expensive than chlorination and disinfection with chloramines. In addition, the chlorite formation will definitely limit the allowable chlorine dioxide dosage in the future since there is no easy solution for it's removal. Granular activated carbon (GAC) filtration was once thought to be an effective method of removal, but is very inefficient in removing chlorites and chlorates. GAC filtration is an expensive proposition regardless and would have only added to the already expensive chlorine dioxide process.

4.3 Possible Solution for Santo Stefano

At Santo Stefano, the primary problem is the loss of disinfectant residual in the water

supplied by ESAF and the need to re-disinfect and maintain compliance under Final Governing Standards. Although ozone can be an excellent primary disinfectant, it provides a residual that lasts only a short period of time. Ozone could be used as a primary disinfectant without the creation of THM's at the ESAF treatment plant, however, chlorine dioxide already serves this purpose. Secondary disinfection, however, is the goal at Santo Stefano. Additionally, the secondary disinfection must be able to last longer than 6.6 days in the U.S. Navy tank under average flow conditions. The alternate disinfectants left to be discussed that hold the key to a possible solution at Santo Stefano are: chlorine, chloramines, and chlorine dioxide.

ClO_2 is being utilized at the main water treatment plant for both pre-disinfection and post-disinfection as shown in the following ESAF water treatment plant schematic.

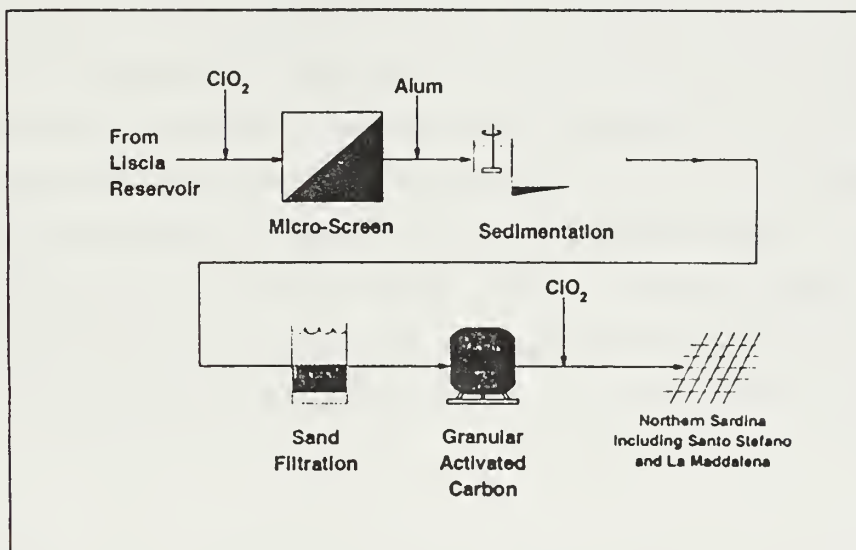


Figure 4.4 – ESAF water treatment plant schematic

It has previously been stated in this report that chlorine dioxide does not maintain a residual as well as free chlorine in a water distribution system. Contrary to what has been published in some texts, however, it can provide a measurable residual that will last in a distribution system. Whether a measurable residual will be provided depends on the characteristics of the water being treated with chlorine dioxide (i.e. is there a significant supply of electron-rich

substances) and the dosage of chlorine dioxide. Singer (1989) has reported that chlorine dioxide residuals exist in the middle and far reaches of the Chesapeake, Virginia water distribution system. In addition Viessman and Hammer, in *Water Supply and Pollution Control*, state that chlorine dioxide is capable of maintaining a residual in a distribution system (Viessman and Hammer, 1998).

This discussion clearly leads to the question – what is the chlorine dioxide residual heading into the U.S. Navy tanks at Santo Stefano? The free chlorine residual at the U.S. Navy tank was measured to be 0.25 mg/l. This free chlorine is from the inefficiencies in the production of chlorine dioxide at the ESAF treatment plant (Figure 4.4). The water quality/quantity survey performed by Malcom Pirnie, Inc. (1996) for the U.S. Navy did not make any effort to measure the chlorine dioxide residual. This is an important oversight for two reasons. The first reason is that there may clearly be a larger disinfectant residual at the inflow to the U.S. Navy tank than is being measured. The second, and more important, reason is that one of the proposed solutions under review by the U.S. Navy currently is GAC adsorption followed by chlorination. Given that chlorite removal by GAC is an inefficient process, this will have to be addressed. Assuming an efficiency rate of 17% (Singer, 1989) free chlorine produced relative to chlorine dioxide, and neglecting free chlorine decay in the system, the post-disinfection ClO_2 dose would be 1.5 mg/l. Additionally, assuming the GAC filtration at ESAF removed all of the chlorite from the pre-disinfection with chlorine dioxide, the chlorite from the post-disinfection with chlorine dioxide could be as high as 80% of this or 1.2 mg/l.

Irregardless of how much chlorine dioxide residual is present, we know that there is currently a sufficient free chlorine residual alone at the U.S. Navy tank influent that secondary disinfection is all that is required. The Italians are meeting CT requirements at the ESAF treatment plant and the residual requirement is being complied with as stated in section 2 of this report. As an aside, a determination of the amount of chlorite ion and chlorine dioxide in the U.S. Navy tank influent can be performed accurately and easily by amperometric titration. There are two alternate disinfectants left to discuss in reference to secondary disinfection – chlorine and chloramines.

Currently, free chlorine is utilized. Sodium hypochlorite is added to the header of each 500 MT (131,650 gal) U.S. Navy tank individually. The amount of free chlorine added is adjusted to maintain a system residual of approximately 0.5 mg/l in the distribution system. Measurements are made at the piers and various locations and the feed rate is adjusted by adjusting the flow of the positive-displacement chlorine feed pump. The problem with this system is that the TTHM formation, as measured at various locations on Santo Stefano, is as high as 100 µg/l. If free chlorine is to be utilized, one method of reducing the THMFP is reducing the pH of the water. Utilizing the THM formation equation developed by Amy et al. (1987) and adjusting the pH while holding constant all other parameters of the previously fit curve (see section 3.4.1), some measure of the ability to reduce the TTHMFP in this manner was determined.

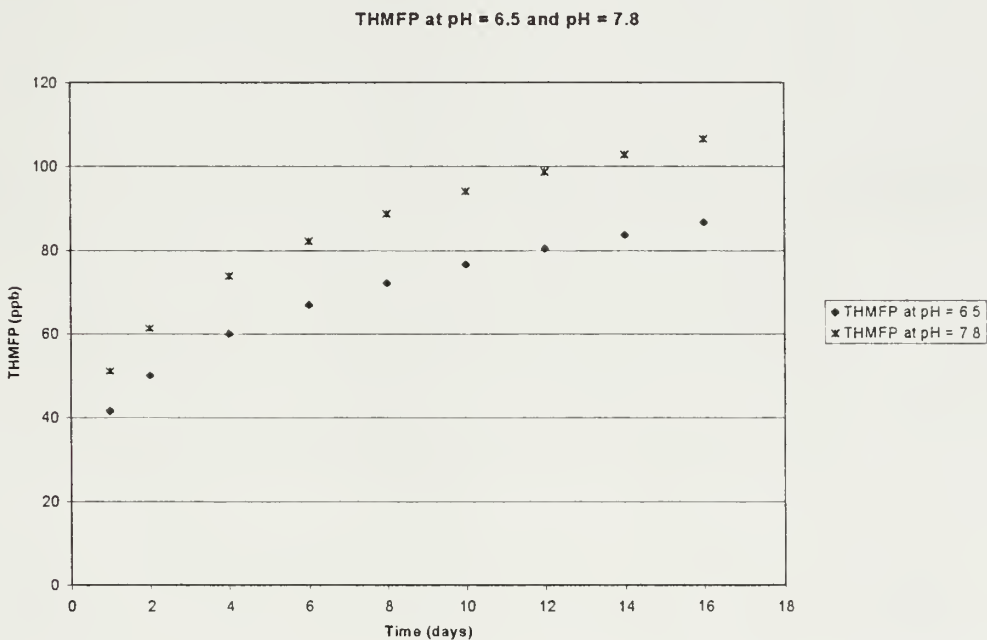


Figure 4.5 – effect of reducing pH from 7.8 to 6.5 on TTHMFP

As can be seen from figure 4.5, the TTHMFP was still almost 90 µg/l after 16 days. In addition, after 1 day the TTHMFP was over 40 µg/l –exceeding the FGS – Italy value of 30

$\mu\text{g/l}$. Since the residence time in the U.S. Navy tanks at Santo Stefano under average flow conditions is 6.6 days, this reduction in TTHMFP will not comply with the FGS.

Perhaps if the residence time in the tanks were reduced or eliminated, a lower dose of Cl_2 could be utilized to prevent exceeding the FGS of $30 \mu\text{g/l}$. To test this, the pH was changed to a more reasonable value of 7 (less corrosive) in the Amy et. al. model and a chlorine dose of 1 mg/l was tested. As in Figure 4.5 the TOC, temperature (T), and UV-254 were all maintained at the measured and estimated values shown in section 3.4.1. The results of this attempt are shown in Figure 4.6 below.

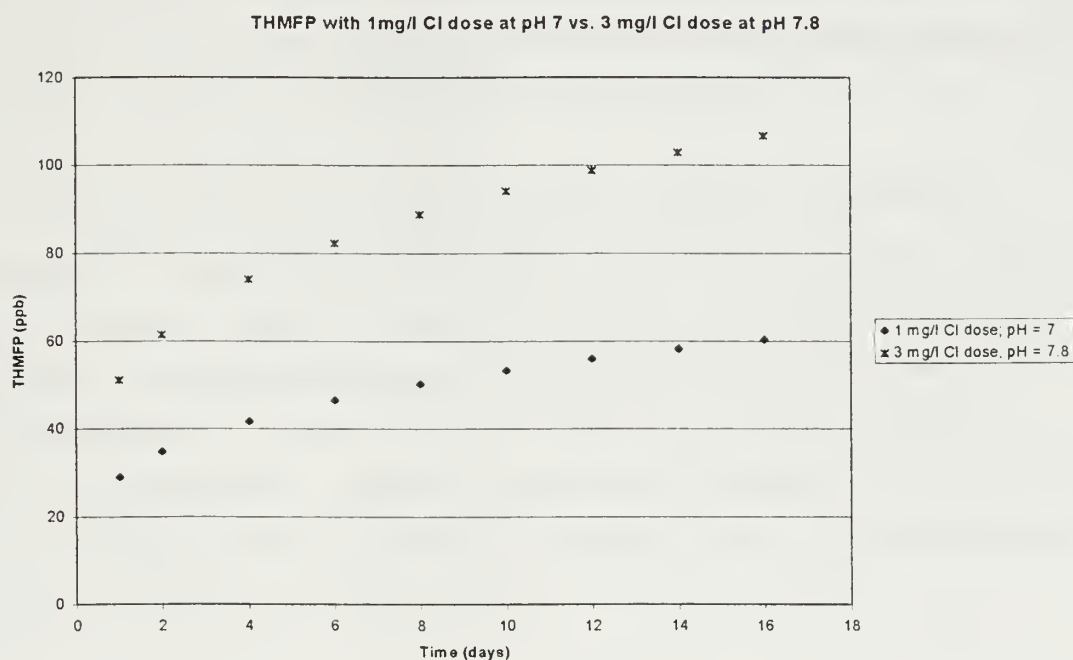


Figure 4.6 – effect of reducing pH to 7 and Cl_2 dose to 1 mg/l on TTHMFP

The 1 mg/l Cl_2 dose was chosen since the chlorine decay in the U.S. Navy tank was measured to be 2.7 mg/l over 14 days. Assuming linear chlorine decay (since not enough data were available to determine an acceptable first order decay the approximate zero order decay was utilized) a decay value can be calculated of $0.008 [\text{mg/l}] \text{ hr}^{-1}$. At this decay rate – 3 days of chlorine decay total approximately 0.6 mg/l . By reducing the detention time in the

tank and small distribution system at Santo Stefano to 3 days, 1 mg/l Cl_2 dose would be more than sufficient.

Clearly from Figure 4.6, however, the retention time in the Santo Stefano system would have to be reduced to less than one day to avoid exceeding the FGS – MCL for TTHM's of 30 ppb. A reduction in retention time of that magnitude is unlikely considering the sporadic water supply to Santo Stefano in the summer tourist season and the critical need for the U.S Navy water supply for homeported submarines, and ships. Since water supply is sometimes unavailable in the summer months, storage must be provided to accept barged water and supplement water needs for these time periods. As discussed in section 1 of this report barges that ship water to Santo Stefano during the high water demand periods are 600 and 1000 MT – limiting how small the storage tanks can be as well.

This leaves chloramines as the final disinfectant to discuss. Application of a chloramine dose of 3 mg/l would last longer than a 3mg/l dose of free chlorine. In tests run on the U.S. Navy tank water at the island of Santo Stefano, a 3-mg/l dose of free chlorine lasted 14 days with a remaining residual of 0.3 mg/l. Under low flow conditions (133 MT/day) the retention time in the 2000 MT U.S. Navy tanks is 15 days. Clearly a chloramine residual could last roughly this length of time if free chlorine did, considering only bulk fluid decay. There would, however, be additional decay of the disinfectant residual in the actual distribution system (Vasconcelos et al., 1997).

The additional decay would be from reactions with the biofilm and reactions involving corrosion of the pipe. Vasconcelos et al. (1997) showed that utilizing only bulk fluid decay to predict decay in the distribution system would underestimate the amount of decay. They determined that the chlorine decay in a Harrisburg, Pa. distribution system was more than could be explained by bulk decay alone. This distribution system contained 30 – 50 year old, unlined iron and steel pipes, which should have given a significant pipe wall demand. Utilizing bulk decay kinetics alone, however, they had a 77% correlation in their data. Even if the wall kinetics account for an additional 30% decay of the chloramines, they would still last longer than 10 days in the Santo Stefano system. For these reasons it would

be recommended that under low flow conditions 2 or 3 of the 4 cells be taken out of service to maintain retention times as low as possible and certainly less than 10 days. During this time periodic maintenance could be performed on these tanks. These tanks would have to be properly disinfected before being placed back on line. Based on the above discussion, if detention times are maintained at less than 10 days, the chloramine residual should last in this distribution system. Only field analysis of the distribution system and a kinetic study could determine the actual allowable detention times.

From the data that are available it is probable that the chloramines would last in the distribution system for approximately 10 days at a dose of approximately 3 mg/l. THM formation must also be considered. The amount of contact time provided for the free chlorine before the addition of ammonia will determine the concentration of THM's. As can

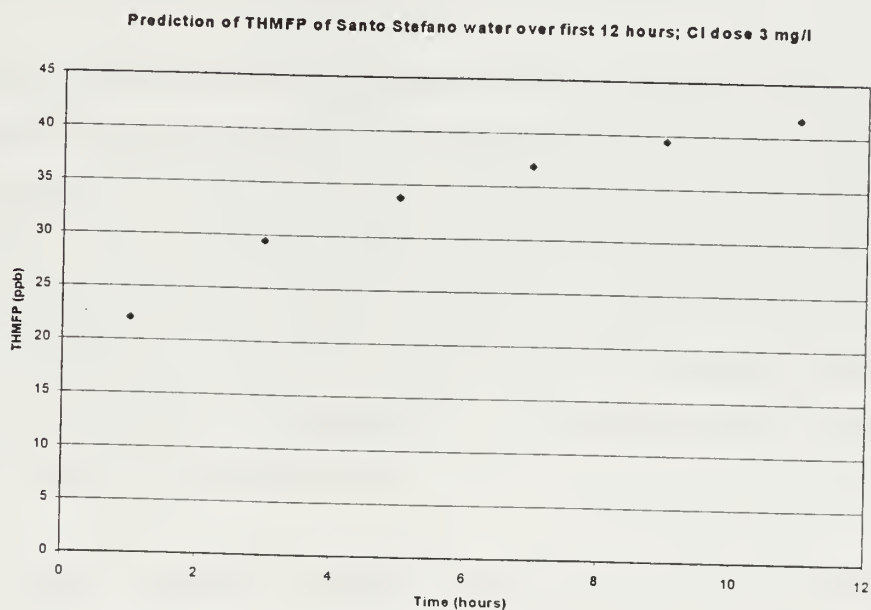


Figure 4.7 – 1 hour free chlorine contact time TTHMFP prediction with 3 mg/l Cl_2 dose at pH = 7.8.

be seen from figure 4.7, 1 hour of free chlorine contact time only has a TTHM concentration of approximately 22 $\mu\text{g/l}$. As shown in table 3.3 this equation was derived by measuring TTHM's at time frames down to 0.1 hour after chlorine dose, so the ability of this model to forecast short timeframe TTHM's is extensive. Further utilization of the Amy et al. model

predicts a TTHMFP of 29 µg/l at 3 hours of free chlorine contact time. The contact time for the free chlorine, therefore, must be limited to approximately 3 hours based on this model prediction.

For secondary disinfection such as what is desirable for Santo Stefano, *concurrent addition* of ammonia and free chlorine could be utilized. *Concurrent addition* is when chlorine and ammonia are added very close to one another in the treatment process. When concurrent addition is accomplished the free chlorine contact time is limited to the time it takes for the chlorine to react with ammonia. This reaction is rapid. At a temperature of 25 °C it is generally a fraction of a second, while at 0 °C it can take up to 5 minutes (Kirmeyer et al. 1993). The degree and speed of mixing also is a factor, however, it can clearly be seen from Figure 4.7 that the TTHM concentration of the water could not exceed 30 ppb within a matter of minutes as predicted by the model.

Preliminary calculations for ammonia and chlorine requirements have been performed and are included in appendix B. For average flow conditions, 1.8 gal/day – 15% solution of NaOCl and 0.09 gal/day 25% aqua ammonia solution would be required. Metering equipment with controls is available to maintain the proper ratio of Cl₂ to NH₃. Typically the ammonia feeder is tied directly to the chlorine residual and the water flow. For preliminary calculations a ratio of 3 to 1 was utilized. Typically the optimum ratio is between 3:1 and 4:1. Each raw water will perform differently and must be evaluated to optimize the formation of monochloramine.

In conclusion, chloramines could be utilized as shown in the distribution system at Santo Stefano to maintain a disinfectant residual while minimizing the formation of THM's. Under lower flow conditions the chloramines would probably last in the system approximately 10 days, however, it would be recommended to operate with lower detention times to improve water quality. This solution is contingent upon water being supplied with a small disinfectant residual. Barged water would be required to be of the same quality. It should be noted that the CT for primary disinfection with chlorine on this water at a chlorine dose of 3 mg/l, pH=8, and T=22°C utilizing table 3-11-1.5 in appendix A is 33.7 minutes. If

primary disinfection were ever required a small tank could be utilized (and level varied with flow) to provide this contact time not in excess of 3 hours without exceeding the FGS – MCL for TTHM's.

5.0 The Treatment Approach

5.1 Reducing the Natural Organic Matter (NOM)

As outlined in section 3.4.2 of this report, the treatment approach to solving the problem of THM formation at Santo Stefano is through the removal of NOM to low enough levels that the THM formation potential (THMFP) is below 30 µg/l as required by the FGS – Italy. As previously stated in section 3.4.2, the most likely means of this removal is the use of GAC adsorption. There will be no attempt in this report to state that this is the only treatment option available. Nor will it be stated that every possible treatment option available has been studied with an in-depth cost and application analysis to say that it is even the best. Clearly, however, GAC adsorption is the most likely selection from a previous track record and technology availability standpoint and will be discussed here.

5.2 Possible Solution for Santo Stefano

Carbon adsorption was defined in section 3.4.2 as the mass transfer of a substance in the liquid phase to the surface of a solid (GAC) where it is bound chemically or physically. Clearly, if enough NOM were adsorbed the THM formation potential of the water could be reduced to below the FGS – Italy value of 30 ppb. In designing a system to remove soluble organics, there are two primary considerations – contact time, and breakthrough characteristics of GAC selected.

Contact time or empty bed contact time (EBCT) is the volume of the adsorber unit containing GAC divided by the flow of fluid through the unit. As EBCT increases the carbon requirement increases. A shorter EBCT results in earlier breakthrough of the carbon (Clark and Lykins 1989). Here breakthrough is defined to occur when the effluent concentration exceeds some preset value. This would seem logical since a shorter EBCT directly translates to a higher loading rate of the organic matter to be removed. For the removal of various substances required EBCT's have been well established. For the removal

of THM precursors an EBCT of 15 –20 minutes is typical (Montgomery Watson, 1998). The point at which breakthrough occurs, for the removal of a particular organic compound, can be approximated by mathematical models. The set point down to what level organic matter must be removed can be field adjusted most accurately for THM precursor removal.

Montgomery Watson has proposed a 35% design to meet the 30-ppb TTHM requirement. The profile of the proposed GAC treatment facility, proposed flow piping additions and preliminary GAC sizing calculations have been included in appendix C. In this preliminary design, the flow to the new GAC facility will be such that unfiltered water will be stored in 3 of the 500 MT tanks. Storage for filtered water will be in the final 500 MT tank. By opening and closing various valves shown on sheet P-2 in appendix C the flow can be adjusted to provide the above arrangement. Storing filtered water in only one tank allows for the use of the remaining tanks to bring in barged water if necessary. In addition, the one filtered tank still provides the elevation pressure head to the water supply so that a hydropneumatic tank is not required to maintain adequate system pressure at Santo Stefano. Further advantages of this design are that the final treated water is stored for much less time. Under average flow conditions less than 2 days.

The proposed GAC units are 2 – 100gpm units containing 90 ft³ of GAC each. This design is based on 15 minutes of contact time at high flow. Peak flow design would have forced usage of a much larger system, but the treated water will be pumped to storage, so during times of higher flow the storage tank can make up for what the GAC units can provide. Backwashing of the GAC filters to remove excess particulate matter would occur when the headloss across the units exceeds a set headloss value. This backwashing will not be allowed to occur at anything other than low flow conditions where 19 to 28 minutes of EBCT is provided. Montgomery Watson performed a mathematical estimation of breakthrough at 130 to 195 days to 50% breakthrough.

The sizing of the GAC units appears flawless. The time to breakthrough here could, however, be seriously overestimated. The mathematical model used to predict the time to

50% breakthrough has the lone variable of TOC concentration in the formula, see equation 5.1.

$$(Eqn 5.1) \quad t_{0.5} = 21,700[TOC]^{-1.3}$$

Where: [TOC] = Concentration of total organic carbon in mg/l
 $T_{0.5}$ = Breakthrough time in bed volumes (BV)

Montgomery Watson used a value of 1.6 mg/l TOC in this equation. It is true that this was the influent U.S. Navy tank value measured by Malcolm Pirnie in 1996, however, the value at the barge filing station was 2.9 mg/l. In addition, Malcolm Pirnie (1996) reported TOC concentrations of 1.9 mg/l and 2.4 mg/l at sites on the island of La Maddalena. A unit run time of as low as 97 days is calculated when a more conservative value of 2 mg/l is utilized (see last page appendix C for conversions).

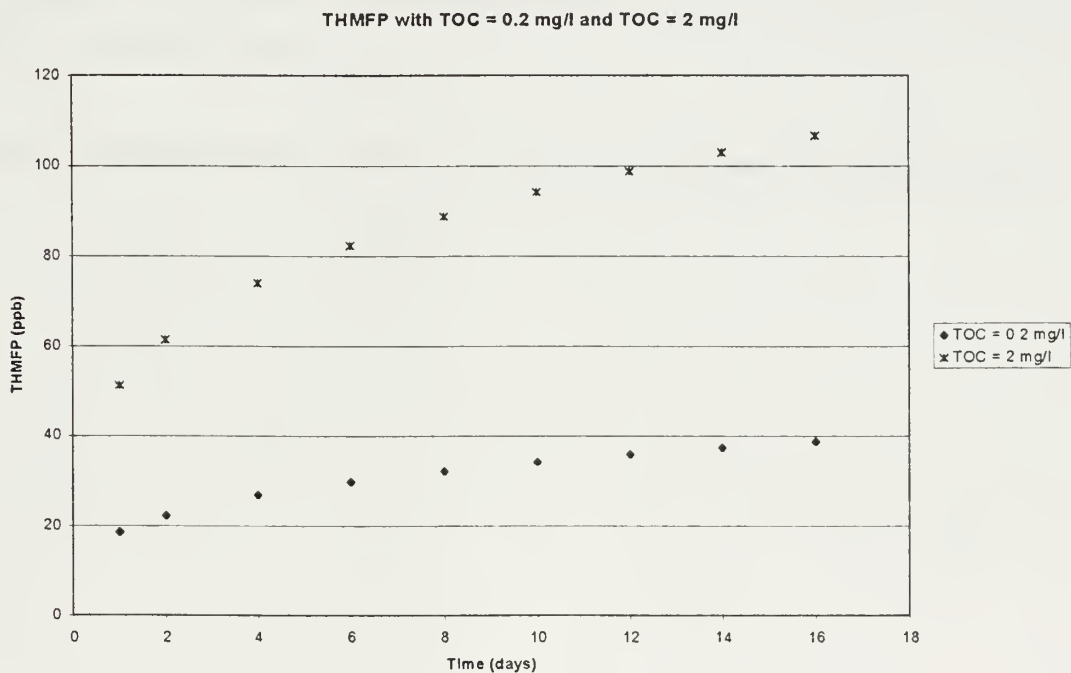


Figure 5.1 – THMFP of water with TOC = 0.2 mg/l and pH = 7.8

Additionally, the Amy et al. model could be utilized to find an approximate TOC level that would have to be reached to maintain a low enough THMFP. The Amy et al. equation was not formulated by chlorinating water with TOC concentrations this low. For this reason, the equation can only provide an approximate prediction of what the TTHMFP might be at such low concentrations of TOC. It should be emphasized that this equation is not a calibrated model and as a result has not been verified to provide predictions in various extreme value ranges accurately. The model was run at a value of 0.2 mg/l at a chlorine dose of 3 mg/l (current chlorination is less than or equal to this value) and is shown in Figure 5.1. Again, all other values in the model were held constant at their previous values shown on page 16 of the report. As can be seen in Figure 5.1, the TTHMFP of the water was still less than 30 ppb at 6 days detention time. For comparison, the model prediction at the original 2 mg/l is shown. The value of 6 days detention time is important since the detention time in the filtered 500 MT tank under low flow conditions is close to 4 days. Allowing some time in the rest of the distribution system, the Amy et. al. model predicts that the TOC needs to be reduced from an initial level of 2 mg/l to 0.2 mg/l. This is a 10% breakthrough rather than a 50% breakthrough. This is likely to reduce the service time of the carbon significantly below the already low value of 97 days.

After a process such as GAC filtration, however, a 3-mg/l dose of chlorine would not

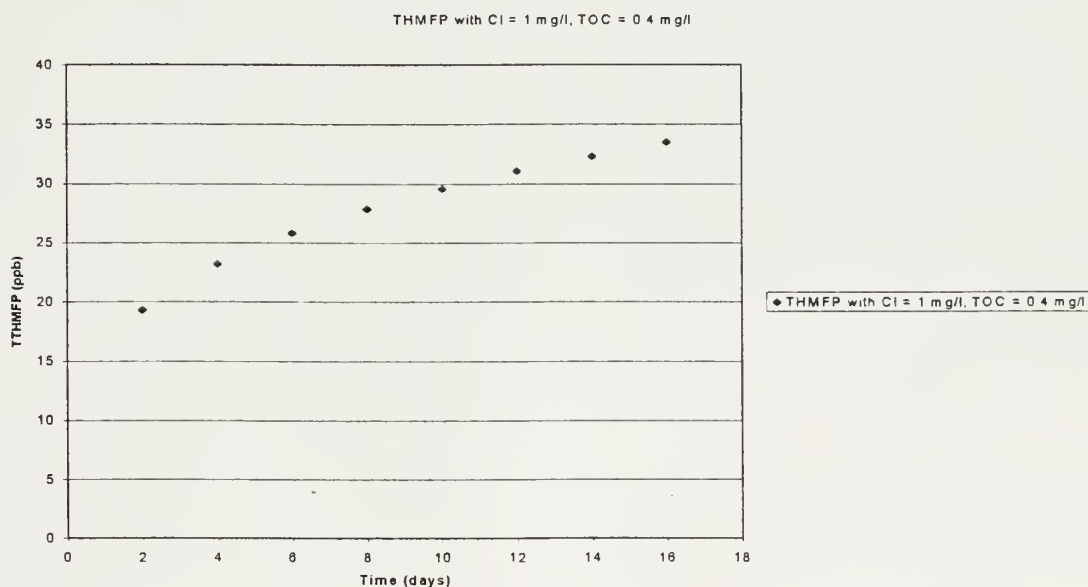


Figure 5.2 – TTHMFP of water with TOC = 0.4 mg/l and pH = 7.8

likely be required since chlorine demand is strongly correlated with TOC concentration. Using a smaller chlorine dose of 1-mg/l in the Amy et al. equation predicts the THM formation with a TOC concentration of 0.4-mg/l shown in Figure 5.2. Reducing TOC concentration from 2-mg/l to 0.4-mg/l requires a 20% breakthrough.

In conclusion, based on the analysis in this report, it would not seem to be an economically feasible process to use GAC. If in fact the model prediction in this report is correct and the TOC concentration must be reduced to 0.2 mg/l or 0.4 mg/l; GAC filtration would likely not be a feasible process at all to reach these low concentrations. In addition iron, manganese and chlorite concentrations will have a further negative impact on GAC performance.

6.0 Conclusions

6.1 DBP Precursor Removal vs. Changes in Disinfection Practice

In this paper two solutions that would reduce THM formation have been presented and discussed. The use of GAC and then filtration has the additional benefit of providing a higher quality water with lower TOC concentrations, however, regeneration of the GAC is likely to be often and is expensive. If the Amy et al. model predictions are correct than GAC filtration will likely not even be able to reduce the TOC concentrations to low enough levels and provide an acceptable reduction in THM formation upon chlorination. The use of chloramines, as outlined in this report should do an effective job of reducing the THM formation to meet FGS, and would be significantly cheaper. Disinfection costs, chlorine and chloramine, are an insignificant cost in water treatment. When processes such as GAC are added, the capital and maintenance costs are highly significant.

Final recommendations are to evaluate the level of chlorite and chlorine dioxide residual in the distribution system. To date, the levels of chlorite have not been determined in any studies. If chlorites are in excess of 1 mg/l, the impact should be determined on GAC filtration. Additionally, if chlorite concentrations are in excess of 1 mg/l, perhaps the Italians could be petitioned to use an alternate secondary disinfectant at the ESAF treatment plant. This could possibly bring the water in compliance with the future D-DBP requirement of maintaining water with less than 1mg/l chlorites and provide a lasting chloramine residual in the system. Since chlorine dioxide production is a more expensive process than chloramines, using an alternate secondary disinfectant might provide a payback as well.

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Appendix A

TABLE 3-11-1.5

**CT VALUES (CT_{99.9}) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLIA CYSTS BY FREE CHLORINE AT 20°C ***

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
0.4	36	44	52	62	74	89	108
0.6	38	45	54	64	77	92	109
0.8	39	46	55	66	79	95	113
1.0	39	47	56	67	81	98	117
1.2	40	48	57	69	83	100	120
1.4	41	49	58	70	85	103	123
1.6	42	50	59	72	87	105	126
1.8	43	51	61	74	89	108	129
2.0	44	52	62	75	91	110	132
2.2	44	53	63	77	93	113	135
2.4	45	54	65	78	95	115	138
2.6	46	55	66	80	97	117	141
2.8	47	56	67	81	99	119	143
3.0	47	57	68	83	101	122	146

* These CT values achieve greater than a 99.99 percent inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the CT_{99.9} values at the lower temperature, and at the higher pH.

TABLE 3-11-1.6

CT VALUES ($CT_{99.9}$) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLIA CYSTS BY FREE CHLORINE AT 25°C AND HIGHER *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
0.4	24	29	35	42	50	59	70
0.6	25	30	36	43	51	61	73
0.8	26	31	37	44	53	63	75
1.0	26	31	37	45	54	65	78
1.2	27	32	38	46	55	67	80
1.4	27	33	39	47	57	69	82
1.6	28	33	40	48	58	70	84
1.8	29	34	41	49	60	72	86
2.0	29	35	41	50	61	74	88
2.2	30	35	42	51	62	75	90
2.4	30	36	43	52	63	77	92
2.6	31	37	44	53	65	78	94
2.8	31	37	45	54	66	80	96
3.0	32	38	46	55	67	81	97

* These CT values achieve greater than a 99.99 percent inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ values at the lower temperature, and at the higher pH.

TABLE 3-11-2

**CT VALUES ($CT_{99.9}$) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLIA CYSTS BY CHLORINE DIOXIDE AND OZONE ***

Agent	Temperature (°C)					
	< 1	5	10	15	20	25
Chlorine Dioxide	63	26	23	19	15	11
Ozone	2.9	1.9	1.4	0.95	0.72	0.48

* These CT values achieve greater than 99.9 percent inactivation of viruses. CT values between the indicated temperatures may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature for determining $CT_{99.9}$ values between indicated temperatures.

Table 3-11-3

**CT VALUES ($CT_{99.9}$) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLIA CYSTS BY CHLORAMINES***

Temperature (°C)						
>1		5	10	15	20	25
Chloramines	3,800	2,200	1,850	1,500	1,100	750

* These values are for pH values of 6 to 9. These CT values may be assumed to achieve greater than 99.99 percent inactivation of viruses only if chlorine is added and mixed in the water prior to the addition of ammonia. If this condition is not met, the system must demonstrate, based on on-site studies or other information that the system is achieving a least 99.99 percent inactivation of viruses. CT values between the indicated temperatures may be determined by linear interpolation. If no interpolation is used, use the CT 99.9 value at the lower temperature for determining $CT_{99.9}$ values between indicated temperatures.

TABLES - CHAPTER 3

TABLE 3-1	
SURFACE WATER TREATMENT REQUIREMENTS	
Unfiltered Systems	
a.	Systems may use unfiltered water if total coliform and/or fecal coliform is less than 50/100 mL [3.4] and 20/100 mL respectively. Systems which use unfiltered surface or groundwater under the direct influence of surface water will analyze the raw water for total coliform or fecal coliforms at least weekly and for turbidity at least daily for a minimum of one year. Filtration must also be applied if turbidity exceeds 1 NTU.
b.	Disinfection must achieve at least 99.9 percent inactivation of <i>Giardia lamblia</i> cysts and 99.99 percent inactivation of viruses by meeting applicable CT values.
c.	Disinfection systems must have redundant components to ensure uninterrupted disinfection during operational periods.
d.	Daily disinfectant residual monitoring immediately after disinfection is required. Disinfectant residual measurements in the distribution system will be made weekly.
e.	Water in a distribution system with a heterotrophic bacteria concentration less than or equal to 500 /ml measured as heterotrophic plate count is considered to have a detectable disinfectant residual.
f.	If disinfectant residuals are undetected in more than 5 percent of monthly samples for two consecutive months, appropriate filtration must be implemented.
Filtered systems	
a.	The turbidity of filtered water will be monitored at least daily.
b.	The turbidity of filtered water will not exceed 1 NTU in 95 percent of the analyses in a month, with a maximum of 5 NTU.
c.	Disinfection requirements are identical to those for unfiltered systems.

HPC < 500/ml
 ⇒ det. residual ✓

TABLE 3-11-1.1

**CT VALUES ($CT_{99.9}$) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLIA CYSTS BY FREE CHLORINE AT 0.5°C OR LOWER***

Free Residual (mg/L)	pH						
	< 6.0	6.5	7.0	7.5	8.0	8.5	9.0
0.4	137	163	195	237	277	329	390
0.6	141	168	200	239	286	342	407
0.8	145	172	205	246	295	354	422
1.0	148	178	210	253	304	365	437
1.2	152	180	215	259	313	376	451
1.4	155	184	221	266	321	387	464
1.6	157	189	228	273	329	397	477
1.8	162	193	231	279	338	407	489
2.0	165	197	236	286	346	417	500
2.2	169	201	242	297	353	426	511
2.4	172	205	247	298	361	435	522
2.6	175	209	252	304	368	444	533
2.8	178	213	257	310	375	452	543
3.0	181	217	286	316	382	460	552

* These CT values achieve greater than a 99.99 percent inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ values at the lower temperature, and at the higher pH.

TABLE 3-11-1.2

**CT VALUES (CT_{99.9}) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLIA CYSTS BY FREE CHLORINE AT 5°C ***

Free Residual (mg/L)	pH						
	<6.0	6.5	7.0	7.5	8.0	8.5	>9.0
0.4	97	117	139	166	198	236	279
0.6	100	120	143	171	204	244	291
0.8	103	122	146	175	210	252	301
1.0	105	125	149	179	216	260	312
1.2	107	127	152	183	221	267	320
1.4	109	130	155	187	227	274	329
1.6	111	132	158	192	232	281	337
1.8	114	135	162	196	238	287	345
2.0	116	138	165	200	243	294	353
2.2	118	140	169	204	248	300	361
2.4	120	143	172	209	253	306	368
2.6	122	146	175	213	258	312	375
2.8	124	148	178	217	263	318	382
3.0	126	151	182	221	268	324	389

* These CT values achieve greater than a 99.99 percent inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the CT_{99.9} values at the lower temperature, and at the higher pH.

TABLE 3-11-1.3

CT VALUES ($CT_{99.9}$) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLIA CYSTS BY FREE CHLORINE AT 10°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
0.4	73	88	104	125	149	177	209
0.6	75	90	107	128	153	183	218
0.8	78	92	110	131	158	189	226
1.0	79	94	112	134	162	195	234
1.2	80	95	114	137	166	200	240
1.4	82	98	116	140	170	208	247
1.6	83	99	119	144	174	211	253
1.8	86	101	122	147	179	215	259
2.0	87	104	124	150	182	221	265
2.2	89	105	127	153	186	225	271
2.4	90	107	129	157	190	230	276
2.6	92	110	131	160	194	234	281
2.8	93	111	134	163	197	239	287
3.0	95	113	137	166	201	243	292

* These CT values achieve greater than a 99.99 percent inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ values at the lower temperature, and at the higher pH.

TABLE 3-11-1.4

CT VALUES ($CT_{99.9}$) FOR 99.9 PERCENT INACTIVATION OF GIARDIA
LAMBLLIA CYSTS BY FREE CHLORINE AT 15°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
0.4	49	59	70	83	99	118	140
0.6	50	60	72	86	102	122	146
0.8	52	61	73	88	105	126	151
1.0	53	63	75	90	108	130	156
1.2	54	64	76	92	111	134	160
1.4	55	65	78	94	114	137	165
1.6	56	66	79	96	116	141	169
1.8	57	68	81	98	119	144	173
2.0	58	69	83	100	122	147	177
2.2	59	70	85	102	124	150	181
2.4	60	72	86	105	127	153	184
2.6	61	73	88	107	129	156	188
2.8	62	74	89	109	132	159	191
3.0	63	76	91	111	134	162	195

* These CT values achieve greater than a 99.99 percent inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ values at the lower temperature, and at the higher pH.

Appendix B

Chloramines

Chlorine Requirement

$$\begin{aligned}\text{Avg. Flow} &= 55 \text{ gpm} = 79,200 \text{ gal/day} \\ &= \underline{.0792 \text{ MG/D}}\end{aligned}$$

$$\begin{aligned}\text{Avg } \text{Cl}_2 \text{ Req'd} &= (3 \text{ mg/l})(.0792 \text{ MG/D})(8.34 \frac{\text{lb/MG}}{\text{mg/l}}) \\ &= \boxed{1.98 \text{ lb/day}}\end{aligned}$$

Utilizing 15% sol'n of NaOCl \rightarrow

$$\frac{1.98 \text{ lb } \text{Cl}_2/\text{day}}{1.1 \text{ lb } \text{Cl}_2/\text{gal } 15\% \text{ NaOCl}} = \boxed{1.8 \text{ gal/day}}$$

Ammonia Requirement

Optimal $\text{Cl}_2 : \text{NH}_3\text{-N}$ Ratio is 3:1

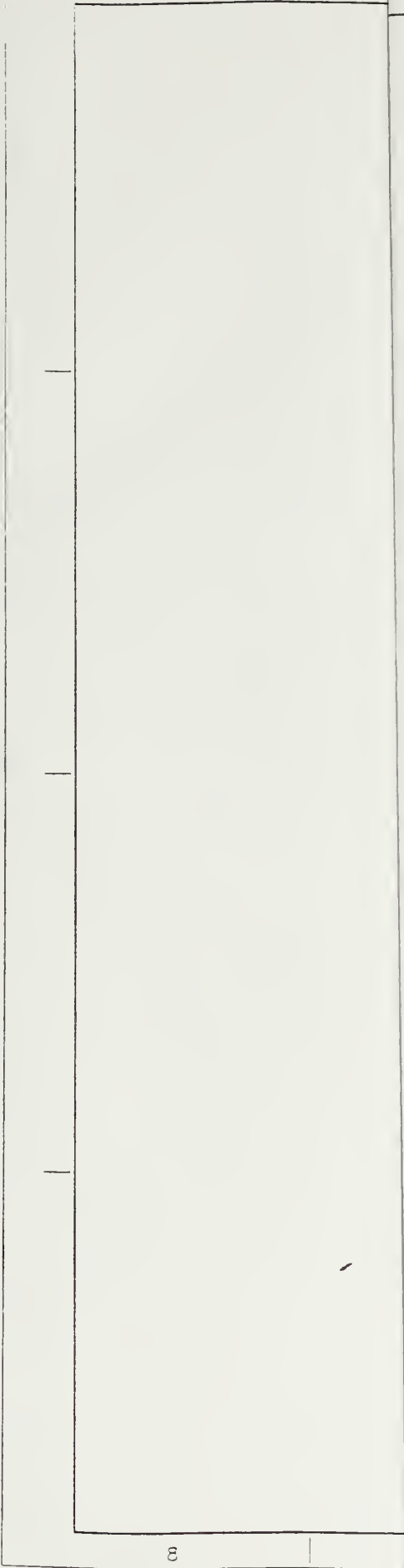
\Rightarrow for 3 mg/l Cl_2 must
have 1 mg/l $\text{NH}_3\text{-N}$

$$\begin{aligned}\text{Avg. } \text{NH}_3 \text{ Req'd} &= (1 \text{ mg/l})(.0792 \text{ MG/D})(8.34 \frac{\text{lb/MG}}{\text{mg/l}}) \\ &= \boxed{.66 \text{ lb/day}}\end{aligned}$$

Using 25% aqua ammonia sol'n \rightarrow

$$\frac{.66 \text{ lb/day}}{7.58 \text{ lb/gal}} = \boxed{0.09 \text{ gal/day}}$$

Appendix C



8



2

DEPARTMENT OF THE NAVY		ATLANTIC DIVISION		NAVAL STATION		MAIN FACILITIES ENGINEERING COMMAND	
LA MADDALENA		WATER TREATMENT FACILITY		SANTO STEFANO, ITALY		ITALY	
EXISTING PIPING SCHEMATIC							
SCALE	77-7777	DATE	77-7777	BY	77-7777	CHKD	77-7777
STA. PROJ. NO.	77-7777	DATE	77-7777	BY	77-7777	CHKD	77-7777
CONTRACT NO.	77-7777	DATE	77-7777	BY	77-7777	CHKD	77-7777
NAVY PROJECT NO.	77-7777	DATE	77-7777	BY	77-7777	CHKD	77-7777
NAVY PROJECT NO.	77-7777	DATE	77-7777	BY	77-7777	CHKD	77-7777
REVISIONS							
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A

REVDATE



BY DHS DATE 4/1/98 CLIENT LANTDIV-NSA LeMuddele SHEET 1 OF 2
 CHKD. BY _____ DESCRIPTION GAC Characteristics JOB NO. 1311035

- Estimate empty bed contact time (EBCT) and loading rate of GAC units

Peak flow = 873 MT/day = 160 gpm (Max flow, 1994-95)
 High flow = 470 MT/day = 86 gpm (90th percentile, 1994-95)
 Average flow = 301 MT/day = 55 gpm (1994-95 data)
 Low flow = 133 MT/day = 24 gpm (25th percentile, 1994-95)

Unit will be sized for 100 gpm. Based on manufacturer's specifications, 100 gpm GAC units may contain 60 to 90 ft³ of GAC (449-673 gals.).

Flow will be split between two GAC units, except under low flow conditions (when units are backwashed or GAC is changed out). Therefore the available GAC volume will be 898 to 1346 gallons.

$$EBCT = \frac{GAC \text{ Volume [gals]}}{Flow [gpm]}$$

Flow Conditions	EBCT (60 ft ³ units)	EBCT (90 ft ³ units)
Low flow, 1 contactor	$\frac{55}{1} = 19 \text{ mins.}$	28 mins
Average flow, 2 contactors	$\frac{202}{2} = 10 \text{ "}$	24 "
High flow, 2 contactors	10 "	16 "
Peak flow, 2 contactors	$\frac{707}{2} = 5.6 \text{ mins}$	8.4 mins.

Typical EBCT for THM precursor removal = 15 to 20 minutes

Peak flow is highly conservative. The second highest flow during 1994-95 was 672 MT/day, 23% lower than the peak flow. Obtaining a 15 minute EBCT for peak flow would require almost doubling the unit size, or the number of units.

High flow conditions are more realistic as a design guide, as the system will be pumping to storage, not meeting instantaneous demand. Unit, with 60 ft³ of GAC media will be undersized with respect to high flow conditions. To achieve 15 min EBCT @ high flow;

$$GAC \text{ Volume} = \left[(15 \text{ min}) (86 \text{ gpm}) \right] = 173 \text{ ft}^3 / 2 = 86.6 \text{ ft}^3 / \text{unit}$$

$$\times \left[\frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right]$$



BY DHS DATE 4/11/98 CLIENT LANTDIV - NSA La Maddalena SHEET 2 OF 2
CHKD. BY _____ DESCRIPTION GAC Characteristics JOB NO. 1311035

$$\text{GAC Unit Surface Loading Rate} = \frac{\text{flow (gpm)}}{\text{r-section area (ft}^2\text{)}}$$

$$\begin{aligned}\text{GAC unit diameter} &= 5 \text{ ft. (typical)} \\ \text{area} &= 19.6 \text{ ft}^2\end{aligned}$$

Flow Conditions		Loading Rate [gpm / ft ²]
Low flow, 1 contactor	$\frac{20 \text{ gpm}}{19.6 \text{ ft}^2}$	1.2
Average flow, 2 units	$\frac{30 \text{ gpm}}{19.6 \text{ ft}^2}$	1.4
High flow, 2 units	$\frac{40 \text{ gpm}}{19.6 \text{ ft}^2}$	2.2
Peak flow, 2 units	$\frac{80 \text{ gpm}}{19.6 \text{ ft}^2}$	4.1



BY DHS DATE 4/1/98 CLIENT LANTDIV - NSA La Maddalena SHEET 1 OF 1
 CHKD. BY _____ DESCRIPTION Estimate GAC change out time JOB NO. _____

Objective: Estimate the run time of GAC units to be installed at Santo Stefano

Based on data developed for the Information Collection Rule (USEPA, 1996), the run time of a GAC unit before breakthrough of TOC equal to 50% of the influent concentration is:

$$t_{0.5} = 21,700 [\text{TOC}]^{-1.3}$$

where $t_{0.5}$ = breakthrough time in bed volumes (BV)

[TOC] = TOC concentration in mg/l

[TOC] = 1.6 mg/l (Malcolm Pirnie, 1996)

$t_{0.5}$ = 11,718 bed volumes.

Unit run time $T = \text{BV} \times \text{EBCT}$

where EBCT = empty bed contact time [mins]
 = 16 to 24 minutes under average flow conditions

$T = 130$ to 195 days to 50% breakthrough

For lower filtered water TOC concentrations, the run time will be lower.

This estimate does not account for the effects of iron and manganese in the GAC media, which will decrease GAC utilization. Chlorine in the unfiltered water will also have a small impact. Therefore the GAC change-out interval will be lower.

@ TOC = 2 mg/l

$$t_{0.5} = 21,700 [2 \text{ mg/l}]^{-1.3} = 8813$$

$$T = \frac{16 \text{ min} (8813) \text{ BV/hr}}{60 \text{ min}} \bigg/ \frac{\text{day}}{24 \text{ hr}} = \boxed{97 \text{ days}}$$

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